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A Theoretical Investigation  
of Hydrogen-Air Reactions

Part I - Behavior with  
Elaborate Chemistry

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TECHNICAL REPORT NO. 250

By P. A. Libby, H. S. Pergament and M. H. Bloom

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# A THEORETICAL INVESTIGATION OF

## HYDROGEN-AIR REACTIONS

### PART I - BEHAVIOR WITH ELABORATE CHEMISTRY \*

By P. A. Libby<sup>1</sup>, H. Pergament<sup>2</sup> and M. H. Bloom<sup>1</sup>

#### SUMMARY

As part of a study of hydrogen-air reactions under conditions of interest in propulsive devices, a theoretical analysis of these reactions with an elaborate description of the chemical behavior considered has been carried out. The system has been idealized so as to result in an adiabatic, isobaric process. In the future, models with simplified chemistry will be treated in order to establish, if possible, a chemical kinetic description which can be employed, with greater ease than the chemical reactions considered in this report, for the treatment of practically interesting flows. The present analysis yields the temperature and composition histories for a range of initial temperatures, mixture ratios and pressures.

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<sup>1</sup> Senior Scientific Investigator

<sup>2</sup> Senior Scientist

## SYMBOLS

A	constants defined by Equation (14)
B	
c	concentration of mixture, mol/cc
$c_i$	concentration of species i, mol/cc
$c_p$	specific heat at constant pressure
h	enthalpy of mixture (defined by Equation (6))
$h_i$	enthalpy of species i
k	reaction rate parameter
$K_p$	equilibrium constant
P	refers to chemical symbol for products in a reaction
p	static pressure
R	refers to chemical symbol for reactants in a reaction
$R_u$	universal gas constant
t	time
T	static temperature
W	molecular weight of mixture (defined by Equation (7))
$W_i$	molecular weight of species i
$\dot{w}_i$	mass rate of formation of species i
X	mole fraction
Y	mass fraction
$\dot{\gamma}_i$	molar rate of formation of species i
$\Delta_i$	enthalpy at reference temperature of species i



$\eta$	equivalence (mixture) ratio
$\nu'$	stoichiometric coefficient of reactant
$\nu''$	stoichiometric coefficient of product
$\rho$	density of mixture
$\tau_1$	denotes end of induction period of reaction
$\tau_2$	denotes end of second period of reaction (see discussion of results)
$\tau_3$	denotes time at which equilibrium is achieved
$\tau_d$	denotes ignition delay time (see discussion of results and Ref. 10)
$\mu$ sec.	microseconds

#### Subscripts

i	pertaining to species i
j	pertaining to species j
m	pertaining to reaction m
0	condition at time $t = 0$
r	reference value

## I INTRODUCTION

The chemical kinetics of hydrogen-air and hydrogen-oxygen reactions have been studied extensively in the past. Reference 1 provides extensive information on these reactions while References 2 and 3 are considered to provide the most recent and accurate data on the mechanism and rate constants for gas phase reactions between hydrogen and oxygen at relatively high temperatures. Most of the studies of this chemical system have been performed in connection with constant volume vessels and have involved significant heterogeneous reactions.

There has recently been considerable interest in this reaction on the part of aeronautical scientists because of the possible use of hydrogen as a fuel in high performance propulsive devices (c.f. References 4-6). These applications involve flow systems in which the chemical and fluid mechanical aspects are intimately related. The limiting models of chemical behavior, i.e., frozen and equilibrium flows, are usually studied first in order to minimize the coupling between the two aspects. Ultimately, however, the selection of the more realistic of these solutions requires simultaneous consideration of the chemical kinetics and fluid mechanics.

The process of the formation of water from hydrogen and oxygen has been found to be complex and to involve many elementary reactions. Indeed, Duff and Schott (References 2 and 3) list the following gas phase reactions:



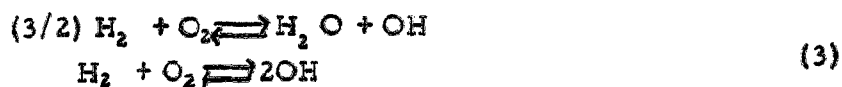


(2)

Equations (1) proceeding to the right describe the bimolecular reactions dominating the early phase of the reaction and Equations (2) proceeding to the right describe the recombination reactions which dominate the final approach to equilibrium. The symbol M in Equations (2) denotes a third body.

In the usual fluid mechanical treatment of the limiting cases of the hydrogen-air reaction in the temperature range from 1000 to 3000°K, it is customary to assume as species present in significant amounts  $O_2$ ,  $H_2$ ,  $H_2O$  and  $N_2$ . Consideration of Equations (1) and (2) indicates that even if nitrogen is considered an inert diluent, there are three additional species, O, H, and OH which must be considered in the study of non-equilibrium flows.

In view of this complexity it is important, for aeronautical applications, to consider simplified but reasonably accurate descriptions of the chemical kinetics of the hydrogen-oxygen reaction. From observations of hydrogen-air flows Fine (Reference 7) deduced an overall reaction rate equation which can be interpreted as



These measurements were roughly in the range of temperatures between 1300 and 2000°K and thus correspond to temperatures of interest in some aeronautical applications (cf. Reference 6). The appearance of the (3/2) factor in Equation (3) indicates, according to the usual chemical usage, that this equation provides an overall description of the production of water.

+L W

If an overall reaction equation of the type given by Equation (3) is found sufficiently accurate, then only one additional species, OH, and two reaction equations need be considered in the treatment of the non-equilibrium fluid mechanics, and coupling between flow and chemical effects can then be taken into account with a reasonable amount of effort.

In order to provide results which can be used to evaluate the accuracy of either Equation (3) or similar approximate descriptions of the reaction, a theoretical investigation of a model problem with the elaborate chemistry of Equations (1) and (2) has been carried out and is described here. In subsequent reports the comparison between the results presented here and the predictions of approximate representations will be given. The fluid mechanical model considered involves a constant pressure, adiabatic system. A homogeneous mixture of hydrogen and air at specified values of the initial temperature, pressure and equivalence ratio, which do not correspond to an equilibrium state, is assumed to prevail at time zero. The subsequent history of the composition and temperature at constant pressure is studied. Note that time "zero" can be associated with a sudden chemically frozen compression or expansion of an equilibrium mixture to the conditions corresponding to the initial state.

This model has several physical interpretations: one corresponds to a chemically inert balloon surrounding a homogeneous gas mixture; the second, to a constant pressure expansion in a nozzle in which the flow is treated as one-dimensional and inviscid; and a third, to the impulsive motion of a piston in a containing cylinder in which the pressure and initial temperature adjustments occur prior to the initiation of the chemical changes. If the pressure is

maintained constant during the reaction in these cases, the mass-velocity is zero or uniform and may be disregarded in the energy balance. If desired, the area distribution of the nozzle or streamtubes can be computed a posteriori. It is of interest to note that these physical interpretations permit the volumetric requirements for the combustion of premixed hydrogen-air reactants to be estimated provided a constant velocity prevails.

This model was selected for theoretical investigation since it corresponds more closely to the conditions of interest in connection with diffusive burning of hydrogen (cf. Reference 6) than the case usually treated by chemical kineticists. Moreover, the model is similar to problems studied by Duff (Reference 2) who determined the reaction profile behind detonation waves in hydrogen-oxygen mixtures diluted in xenon. However, such reaction zones involve significant changes in both velocity and pressure during the period of reaction. It should be noted that if the initial state is assumed to be achieved by a strong shock, the pressure alterations downstream of the shock will be small and the model employed here will be approximately valid. This shock in general will not satisfy the Chapman-Jouguet condition but can be created, for example, by the high speed motion of a blunt body through a hydrogen-air mixture.

In this analysis it is assumed that the maximum temperatures are sufficiently low so that nitrogen may be considered an inert diluent, i.e., the dissociation of nitrogen and the formation of nitric oxide and ammonia are neglected. Thus the species considered are  $O_2$ ,  $H_2$ ,  $H_2O$ ,  $N_2$ ,  $O$ ,  $H$  and  $OH$ ; these will be denoted respectively by subscripts  $i = 1, \dots, 7$ .

In the following section the theoretical analysis is described while in the final sections the numerical results and conclusions are discussed.

The authors are pleased to acknowledge that Dr. Antonio Ferri suggested that the problem be studied and Mr. D. Magnus and Miss J. Connolly assisted in programming and carrying out the calculations.

## II. ANALYSIS

The basic equations describing the behavior of the gas idealized according to the model described in the Introduction are

$$dY_i/dt = \dot{w}_i/\rho = W_i \dot{\gamma}_i/\rho, \quad i = 1, 2, \dots, 7 \quad (4)$$

$$\rho = (pW/R_u T) \quad (5)$$

$$h = \sum_{i=1}^7 Y_i h_i = \left( \sum_{i=1}^7 Y_i h_i \right)_0 \quad (6)$$

$$W = \left( \sum_{i=1}^7 Y_i / W_i \right)^{-1} = \sum_{i=1}^7 X_i W_i \quad (7)$$

Auxiliary equations of the form

$$\sum_{i=1}^7 Y_i = 1, \quad \sum_{i=1}^7 \dot{\gamma}_i W_i = 0 \quad (8)$$

$$\dot{\gamma}_i = \dot{\gamma}_i(c_j, T), \quad i, j = 1, 2, \dots, 7 \quad (9)$$

$$h_i = h_i(T) \quad (10)$$

$$c_i = \rho Y_i / W_i \quad (11)$$

complete the system of equations. The initial conditions are: at  $t = 0$ ,

$$T = T_0, \quad Y_i = Y_{i,0}.$$

Consider the detailed expressions for the  $\dot{\gamma}_i$ 's; first, with nitrogen assumed to be inert,  $\dot{\gamma}_4 \equiv 0$  and  $Y_4 \equiv Y_{4,0}$ . Next, since the activation energy of the first reaction equation in the system given by Equation (1) is considerably larger than the others, it is reasonable to neglect this reaction and to consider only the last eight reactions. The rate constants for the forward reaction, i.e., in the direction to the right in the Equations (1) and (2), are denoted  $k_m$ ,  $m = 1, 2, \dots, 8$  while the corresponding backward constants are denoted  $k_m$ ,  $m = 9, 10, \dots, 16$ . The general expression for  $\dot{\gamma}_i$  is then (cf. Reference 8)

$$\dot{\gamma}_i = \sum_{m=1}^{16} (\nu_{i,m}'' - \nu_{i,m}') k_m \prod_{j=1}^7 c_j^{\nu_{j,m}'} , \quad i, j \neq 4 \quad (12)$$

for the general reaction  $\sum_i \nu_i' R_i \rightarrow \sum_i \nu_i'' P_i$

The values of the rate constants for the forward reactions were taken from Schott (Reference 3); those for the backward reactions were computed from the equilibrium constants corresponding to each elementary reaction. Thus (cf. Reference 8)

$$k_m = k_{m-8} K_{p,m}^{-1} (R_u T)^{\Delta n, m} \quad (13)$$

where  $m = 9, 10, \dots, 16$  and  $\Delta n, m = \sum_{i=1}^7 (\nu_{i,m}'' - \nu_{i,m}')$

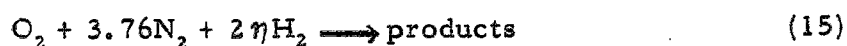
The equilibrium constant  $K_{p,m}$  in Equation (13) was approximated in the form



$$K_{p,m} = B_m e^{A_m/T}$$

over the temperature range  $1000^\circ\text{K} < T < 3000^\circ\text{K}$ ; the requisite values of  $K_{p,m}$  being computed by application of the tables in Reference 8. In Table I and Appendix I there are presented, respectively, the values for  $k_m$  and the explicit relations for the  $\dot{\gamma}_i$ 's used for this analysis. The third bodies in the recombination reactions given by Equations (2) were taken to be all species present.

Consider next the determination of the initial conditions. It is assumed that at time zero the atomic hydrogen and atomic oxygen are in equilibrium with  $\text{H}_2$  and  $\text{O}_2$  respectively. Moreover, neither water nor hydroxyl radical is assumed present so that at  $t = 0$ ,  $Y_3 = Y_7 = 0$ . The initial concentrations of molecular oxygen and molecular hydrogen and the constant concentration of nitrogen are conveniently expressed in terms of the equivalence ratio  $\eta$  defined by the chemical equation



Thus a value of  $\eta = 1$  corresponds to stoichiometric proportions of hydrogen and oxygen. In terms of  $\eta$  the remaining initial conditions are

$$\begin{aligned} Y_{1,0} &= 32/(137.3 + 4\eta) \\ Y_{2,0} &= 4\eta/(137.3 + 4\eta) \\ Y_{4,0} &= 105.3/(137.3 + 4\eta) \end{aligned} \quad (16)$$

Clearly this does not imply equilibrium of the entire mixture in the initial state.

Now Equation (16) along with the stated initial conditions on  $Y_3$  and  $Y_7$  permit the approximate initial concentrations,  $Y_{5,0}$  and  $Y_{6,0}$  to be obtained from the equilibrium constants for the dissociation of molecular oxygen and hydrogen respectively.

It is noted that other treatments of the initial conditions could have been employed. For example, it could have been assumed that  $Y_3 = Y_5 = Y_6 = Y_7 = 0$  at  $t = 0$ . Since the first reaction in Equation (1) was neglected, the reaction would, in this case, be initiated by dissociation of  $H_2$  and  $O_2$  followed by the chain reactions leading to the formation of OH, and additional O and H. It is believed that this treatment would alter only the induction period described below and would not affect significantly the overall reaction history.

Numerical analysis requires analytic representation of the static enthalpy-temperature relations corresponding to Equation (10). For the limited temperature range of interest in this study, it will be sufficiently accurate to let

$$h_i = \Delta_i + \bar{c}_{p_i}(T - T_r) \quad (10a)$$

where  $T_r$  is a reference temperature in the range of interest and  $\Delta_i$  and  $\bar{c}_{p_i}$  are constants so that the exact  $h_i = h_i(t)$  relation is closely approximated. The assumption attendant with Equation (10a) implies rigorously a frozen vibrational energy at some mean temperature. Equation (10a) can be employed in Equation (6) to yield the following explicit expression for the temperature:

$$T = T_r + \left[ \sum_{i=1}^7 Y_i \left[ \Delta_i + \bar{c}_{p_i} (T - T_r) \right] \right] - \sum_{i=1}^7 Y_i \Delta_i \left[ \sum_{i=1}^7 Y_i \bar{c}_{p_i} \right]^{-1} \quad (6a)$$

The analysis required for numerical determination of the history of a mixture of hydrogen and air according to the model under consideration has now been presented. A particular problem is specified by values of the pressure  $p$ , the initial temperature  $T_0$ , and the equivalence ratio  $\eta$ .

The numerical integration was carried out on an IBM 7090 employing the standard fourth order Runge-Kutta method for starting the calculations and the Adams-Moulton predictor-corrector technique for the continuing integration. The solution of the differential equations was obtained to times of roughly  $2(10^{-4})$  seconds or more, or until the temperature became essentially constant with time.

It is noted that while in principle the numerical integration may be carried out in terms of five differential equations with the sixth unknown mass fraction determined from the equation  $\sum_{i=1}^7 Y_i = 1$ , the mass fractions initially differ by several orders of magnitude so that the problem was formulated as one involving six differential equations and the summation condition was considered a check in the accuracy of the results.\*

The cases studied are given in Table II along with the mass fraction  $Y_4$  in each case. The following constants were employed:

---

\*It was found that the summation was  $1 \pm 10^{-5}$ . Note that if the element mass fractions are considered, only four differential equations need be considered. However, the same objection concerning accuracy applies.

$$\Delta_1 = 185.23 \text{ cal/gm}$$

$$\Delta_2 = 2687.9 \text{ cal/gm}$$

$$\Delta_3 = -2831.3 \text{ cal/gm}$$

$$\Delta_4 = 200.05 \text{ cal/gm}$$

$$\Delta_5 = 3938.1 \text{ cal/gm}$$

$$\Delta_6 = 55,873.0 \text{ cal/gm}$$

$$\Delta_7 = 911.78 \text{ cal/gm}$$

$$W_1 = 32$$

$$W_2 = 2$$

$$W_3 = 18$$

$$W_4 = 28$$

$$W_5 = 16$$

$$W_6 = 1$$

$$W_7 = 17$$

$$\bar{c}_{p1} = .26403 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p2} = 3.654 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p3} = .56361 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p4} = .28382 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p5} = .3121 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p6} = 4.968 \text{ cal/gm } ^\circ\text{K}$$

$$\bar{c}_{p7} = .43765 \text{ cal/gm } ^\circ\text{K}$$

$$T_r = 1060^\circ\text{K}$$

$$R_u = 82.06 \text{ cc-atmos/mole } ^\circ\text{K}$$

### III PRESENTATION AND DISCUSSION OF RESULTS

The results of the cases studied, as listed in Table II, are presented as time histories of the temperature and mass fractions. In Figures 1a to 1d, the temperature histories are given while in Figures 2a to 2d through 8a to 8d, the histories of the mass fractions  $Y_1$  through  $Y_7$  are presented.

The history of the reaction can be characterized by three periods. Consider qualitatively these results; first, there exists an induction period during which there are significant increases in the mass fractions of O, H, and OH not observable from the graphs but given by the computer results. At the end of this induction period, denoted as  $\tau_1$ , there occurs a second period during which a rapid change in composition occurs with relatively little change in static temperature. The mass fractions of  $O_2$ ,  $H_2$  and  $H_2O$  come close to their equilibrium values during this second period. However, small but significant amounts of atoms, O and H, and of hydroxyl radicals OH are created; these amounts are in excess of their equilibrium values. Since the enthalpy per unit mass associated with the atomic hydrogen is from 20 to 200 times larger than that of any other species, this is by far the most important intermediate in the system under consideration. The time corresponding to the end of this second period is denoted  $\tau_2$ . During the final and most extended period of the reaction, the concentrations of the intermediates decay to their equilibrium values and the heat release associated with the recombination of O and H and the decay of OH leads to the temperature rise. The time at which equilibrium is essentially achieved will be denoted  $\tau_3$ . This general scheme for the reaction is substantially the same as that indicated by Duff, Schott and co-workers (References 2, 3 and 9) for the reaction profile behind a detonation wave.

Consider more quantitatively the numerical results. Given in Table III are the times  $\tau_i$ ,  $i = 1, 2, 3$  for the various cases; these were estimated by examining the time history of the mass fraction of H. The time  $\tau_1$  was selected at the time when an observable amount of H appeared on the graphs (Figures 6a-d); this was  $Y_6 \approx 10^{-4}$ . The time  $\tau_2$  was taken to correspond to the peak in  $Y_6$  and the time  $\tau_3$ , when available, was determined by  $dY_6/dt \approx 0$ .

The ignition delay time denoted here by  $\tau_d$  and predicted by the approximate theoretical analysis of Nicholls (Reference 10) has been interposed between the columns for  $\tau_1$  and  $\tau_2$  in Table III. This time is defined as that corresponding to an inflection point in the curve giving the time-history of  $Y_6$  and thus should be between  $\tau_1$  and  $\tau_2$ . The equation for  $\tau_d$  in the notation and with the rate constants used herein is\*

$$\tau_d = \left[ R_u T_o / 6X_{1,0} p (10^{14}) \right] e^{8810/T_o} \left[ \ln(X_{1,0}/X_{2,0}) + \ln 3 + 26340/T_o \right] \quad (17)$$

where  $T_o$  is in degrees Kelvin,  $p$  is in atmospheres and  $R_u = 82.06$  cc-atm/mole-°K.

Consideration of the results in Table III indicates that within a factor of two, Equation (17) predicts, in most cases, a time within the second period of the chemical reaction. In addition, the times  $\tau_2$  shows a dependence on pressure and  $X_{1,0}$  in satisfactory agreement with either Equation (17) or Equation (17a)\*\*. Thus, the approximate analysis of Nicholls can be employed to give the dependence on pressure, temperature and oxygen concentration of the times characterizing the early phases

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\* Note that the first reaction in Equation (1) was considered by Nicholls; the value given by Schott (Reference 3) for the rate constant was used in Equation (17). It is thus implicitly assumed that this first reaction alters only slightly the time-history of the composition.

\*\* Note that  $X_{1,0} = (4.76 + 2\eta)^{-1}$

of the reaction ; indeed, the second bracketed term in Equation (17) is roughly constant for the initial conditions studied here, so that roughly

$$T_d \sim \frac{T_o e^{8810/T_o}}{X_{1,0} p} \quad (17a)$$

There seems to be no equivalent analysis for the estimation of the overall time  $\tau_3$ ; indeed, one of the desired results of the studies of chemical models would be a ready estimate of this overall time. It should be noted, however, that  $\tau_3$  is 20 to 40 times greater than  $\tau_2$ . This result must be recognized if the ignition time delay is used as a measure of the chemical time as, for example, in Reference 6. The extent of this third period, during which the heat release and recombination occur, implies that the overall reaction time is sensitive to the pressure, roughly  $\tau_3 \sim p^{-2}$ . Thus the importance of pressure on the overall reaction time is emphasized.

There are shown in Figures 1b-d the flame temperatures given by Reference 11: the asymptotic temperatures given by numerical integration should equal these flame temperatures. It will be seen that the agreement is good, so that the assumptions with respect to the products and to the enthalpy-temperature relations may be considered satisfactory.

It is perhaps worth noting that for the initial conditions corresponding to Case 7 ( $p = 1$  atmosphere,  $T_o = 1600^\circ K$ ,  $\eta = 1.8$ ) the reaction is complete in roughly  $200 \mu \text{ sec.}$ ; thus, if a mean velocity of  $20,000 \text{ ft/sec.}$  is assumed, a combustion chamber length of four feet would be required to achieve complete combustion.

#### IV CONCLUDING REMARKS

A study has been made of the reaction history of hydrogen-air mixtures under adiabatic, isobaric conditions. An elaborate chemistry has been treated herein with a view toward establishing rather accurate reaction histories. In the future, simplified chemical models will be considered and the reaction histories based thereon compared to those presented here. These models will then permit approximate analyses of the non-equilibrium behavior of hydrogen-air mixtures under flow conditions as, for example, in exhaust nozzles and mixing regions.

The results presented for a variety of initial temperatures, pressures and mixture ratios indicate that during the early phases of the reaction the main products achieve close to their equilibrium values with little change in temperature. However, the intermediates, atomic oxygen, atomic hydrogen, and the hydroxyl radical exceed their equilibrium values. The remaining, major portion of the reaction time involves the decay of these intermediates and the chemical energy release associated therewith. Because of its thermodynamic importance, i.e., its large enthalpy per unit mass, atomic hydrogen appears to be the most important intermediate for the reaction considered.



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TABLE I - RATE CONSTANTS

<u>m</u>	<u>Reaction</u>	<u>k<sub>m</sub><sup>*</sup></u>
1	$\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$	$3 \times 10^{14} e^{-8810/T}$
2	$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$	$3 \times 10^{14} e^{-4030/T}$
3	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$3 \times 10^{14} e^{-3020/T}$
4	$2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$3 \times 10^{14} e^{-3020/T}$
5	$2\text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	$1 \times 10^{15}$
6	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$1 \times 10^{16}$
7	$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	$1 \times 10^{15}$
8	$2\text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$3 \times 10^{14}$
9	$\text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2$	$2.48 \times 10^{13} e^{-660/T}$
10	$\text{OH} + \text{H} \rightarrow \text{O} + \text{H}_2$	$1.3 \times 10^{14} e^{-2490/T}$
11	$\text{H}_2\text{O} + \text{H} \rightarrow \text{OH} + \text{H}_2$	$1.33 \times 10^{15} e^{-10,950/T}$
12	$\text{H}_2\text{O} + \text{O} \rightarrow 2\text{OH}$	$3.12 \times 10^{15} e^{-12,510/T}$
13	$\text{H}_2 + \text{M} \rightarrow 2\text{H} + \text{M}$	$\frac{1.85 \times 10^{19}}{T} e^{-54,000/T}$
14	$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	$\frac{9.66 \times 10^{20}}{T} e^{-62,200/T}$
15	$\text{OH} + \text{M} \rightarrow \text{H} + \text{O} + \text{M}$	$\frac{8 \times 10^{18}}{T} e^{-52,500/T}$
16	$\text{O}_2 + \text{M} \rightarrow 2\text{O} + \text{M}$	$\frac{2.9 \times 10^{19}}{T} e^{-60,600/T}$

\* k<sub>5</sub>-k<sub>8</sub> have units (moles/cc)<sup>-2</sup> sec<sup>-1</sup>

all other k<sub>m</sub> have units (moles/cc)<sup>-1</sup> sec<sup>-1</sup>

TABLE II  
INITIAL CONDITIONS FOR CASES STUDIED

Case	p, atmospheres	T <sub>0</sub> , °K	$\eta$	Y <sub>4</sub>
1	0.1	1600	0.2	0.76249
2	0.1	1600	1.8	0.72872
3	1	1400	0.2	0.76249
4	1	1400	1.8	0.72872
5	1	1600	0.2	0.76249
6	1	1600	1.0	0.74522
7	1	1600	1.8	0.72872
8	1	1115	0.4	0.75810
9	1	1155	0.8	0.74947
10	1	1187	1.2	0.74103
11	1	1211	1.6	0.73278

TABLE III  
TIMES FOR PERIOD IN REACTION HISTORY

Case	$\tau_1$	$\tau_d$	$\tau_2$	$\tau_3$
1	10	52	27	
2	10	74	52	
3	3.4	11	7.0	
4	5.0	14	12	300
5	2.5	5.2	3.4	
6	1.6	1.3	3.8	
7	1.8	1.1	5.4	200
8	25	68	39	
9	22	49	32	700
10	17	44	29	
11	16	41	28	

All times are in microseconds

APPENDIX I

EXPRESSIONS FOR  $\dot{\gamma}_i$  USED IN EQUATION (4)

$$\dot{\gamma}_1 = -k_1 c_6 c_1 + k_9 c_7 c_5 + k_8 c_5^2 c - k_{16} c_1 c$$

$$\dot{\gamma}_2 = -k_2 c_5 c_2 + k_{10} c_7 c_6 - k_3 c_7 c_2 + k_{11} c_3 c_6 + k_5 c_6^2 c - k_{13} c_2 c$$

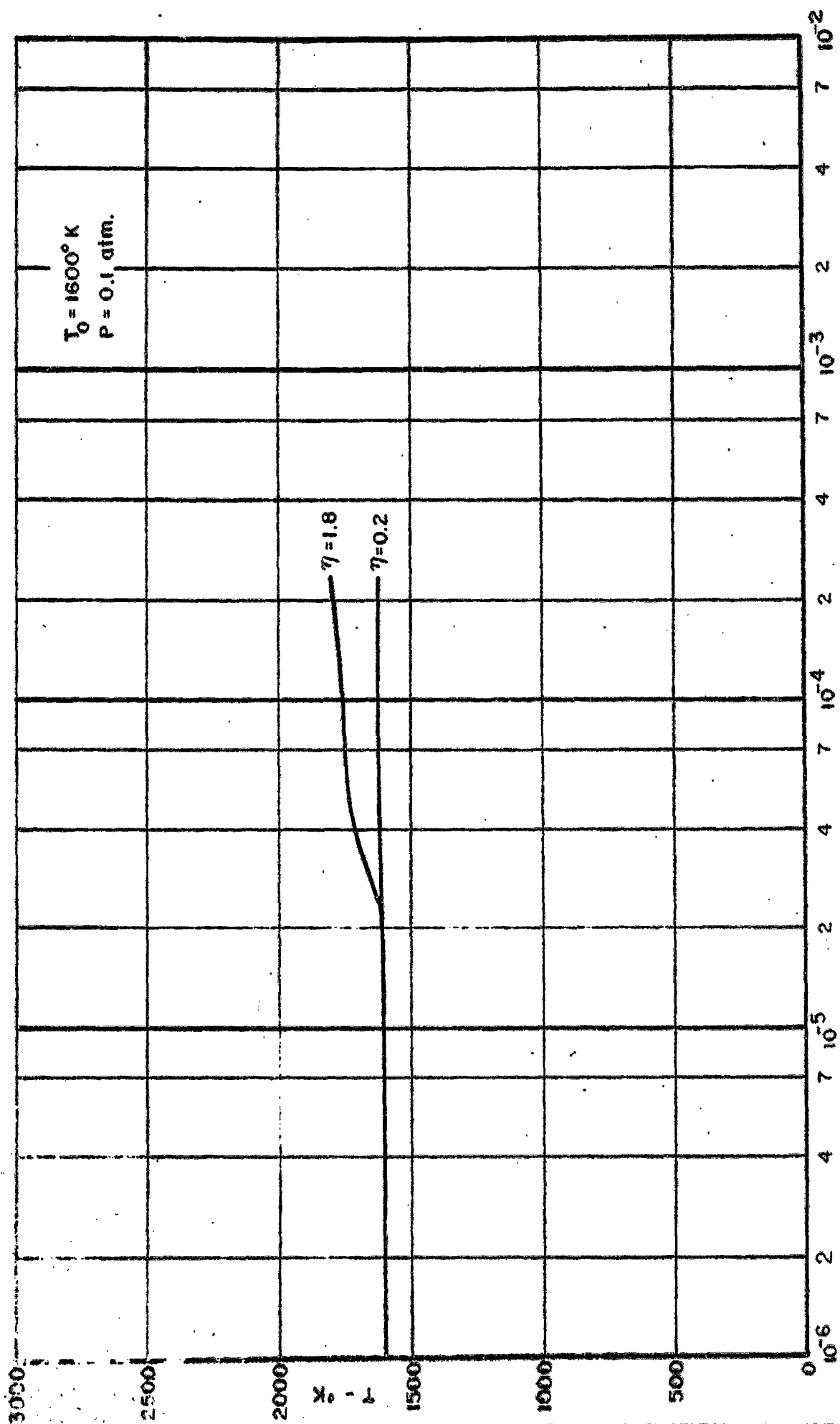
$$\dot{\gamma}_3 = k_3 c_7 c_2 - k_{11} c_3 c_6 + k_4 c_7^2 - k_{12} c_3 c_5 + k_6 c_6 c_7 c - k_{14} c_3 c$$

$$\dot{\gamma}_4 = 0$$

$$\begin{aligned} \dot{\gamma}_5 = & k_1 c_6 c_1 - k_9 c_7 c_5 - k_2 c_5 c_2 + k_{10} c_7 c_6 + k_4 c_7^2 - k_{12} c_3 c_5 \\ & - k_7 c_6 c_5 c + k_{15} c_7 c - 2k_8 c_5^2 c + 2k_{16} c_1 c \end{aligned}$$

$$\begin{aligned} \dot{\gamma}_6 = & -k_1 c_6 c_1 + k_9 c_7 c_5 + k_2 c_5 c_2 - k_{10} c_6 c_7 + k_3 c_7 c_2 \\ & - k_{11} c_3 c_6 - 2k_5 c_6^2 c + 2k_{13} c_2 c - k_6 c_6 c_7 c \\ & + k_{14} c_3 c - k_7 c_6 c_5 c + k_{15} c_7 c \end{aligned}$$

$$\begin{aligned} \dot{\gamma}_7 = & k_1 c_6 c_1 - k_9 c_7 c_5 + k_2 c_5 c_2 - k_{10} c_7 c_6 - k_3 c_7 c_2 \\ & + k_{11} c_3 c_6 - 2k_4 c_7^2 + 2k_{12} c_3 c_5 - k_6 c_6 c_7 c \\ & + k_{14} c_3 c + k_7 c_6 c_5 c - k_{15} c_7 c \end{aligned}$$



TIME - SECONDS

FIG. 1 TEMPERATURE HISTORY  
a) CASES 1 AND 2

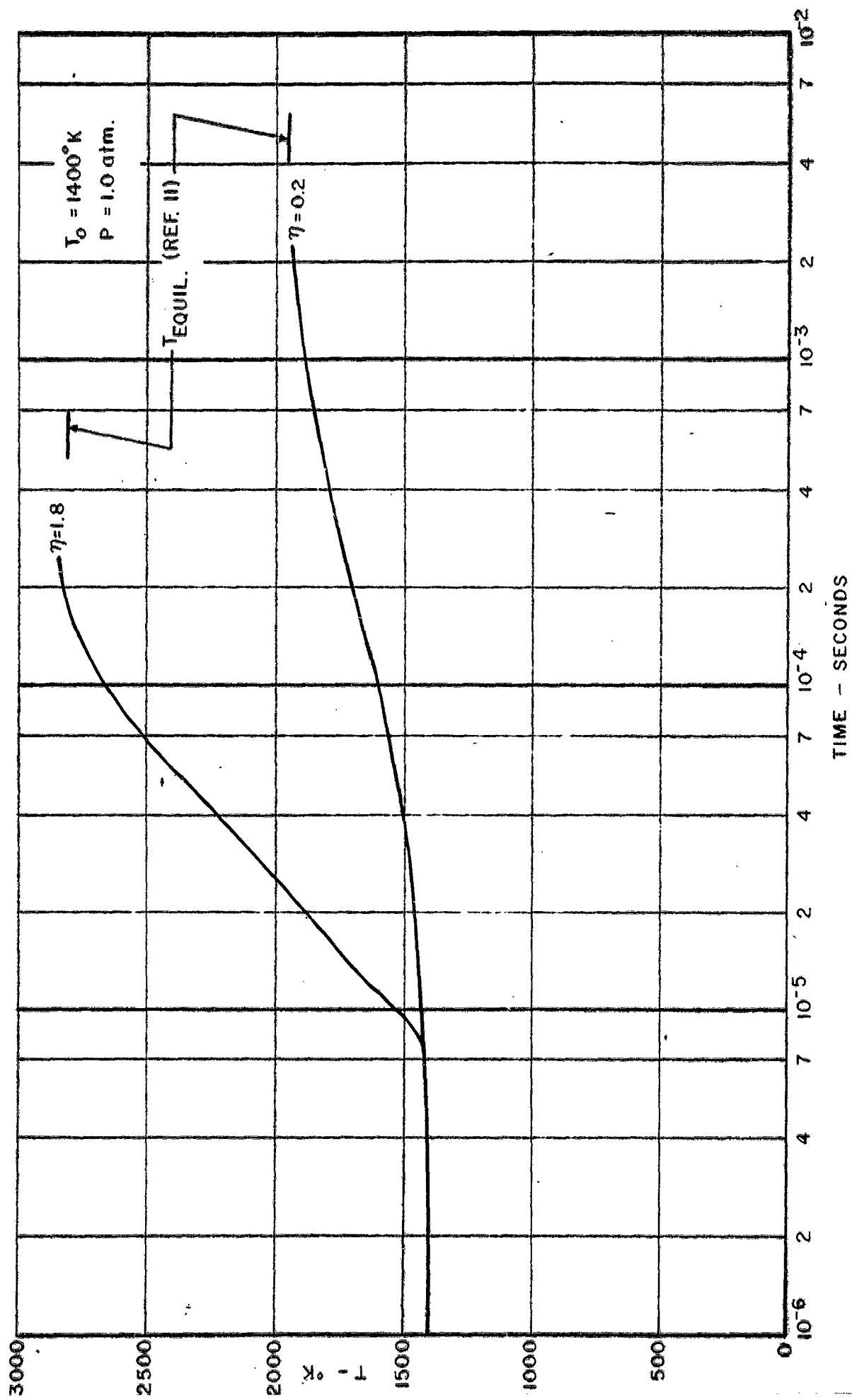


FIG. 1 TEMPERATURE HISTORY  
 b) CASES 3 AND 4

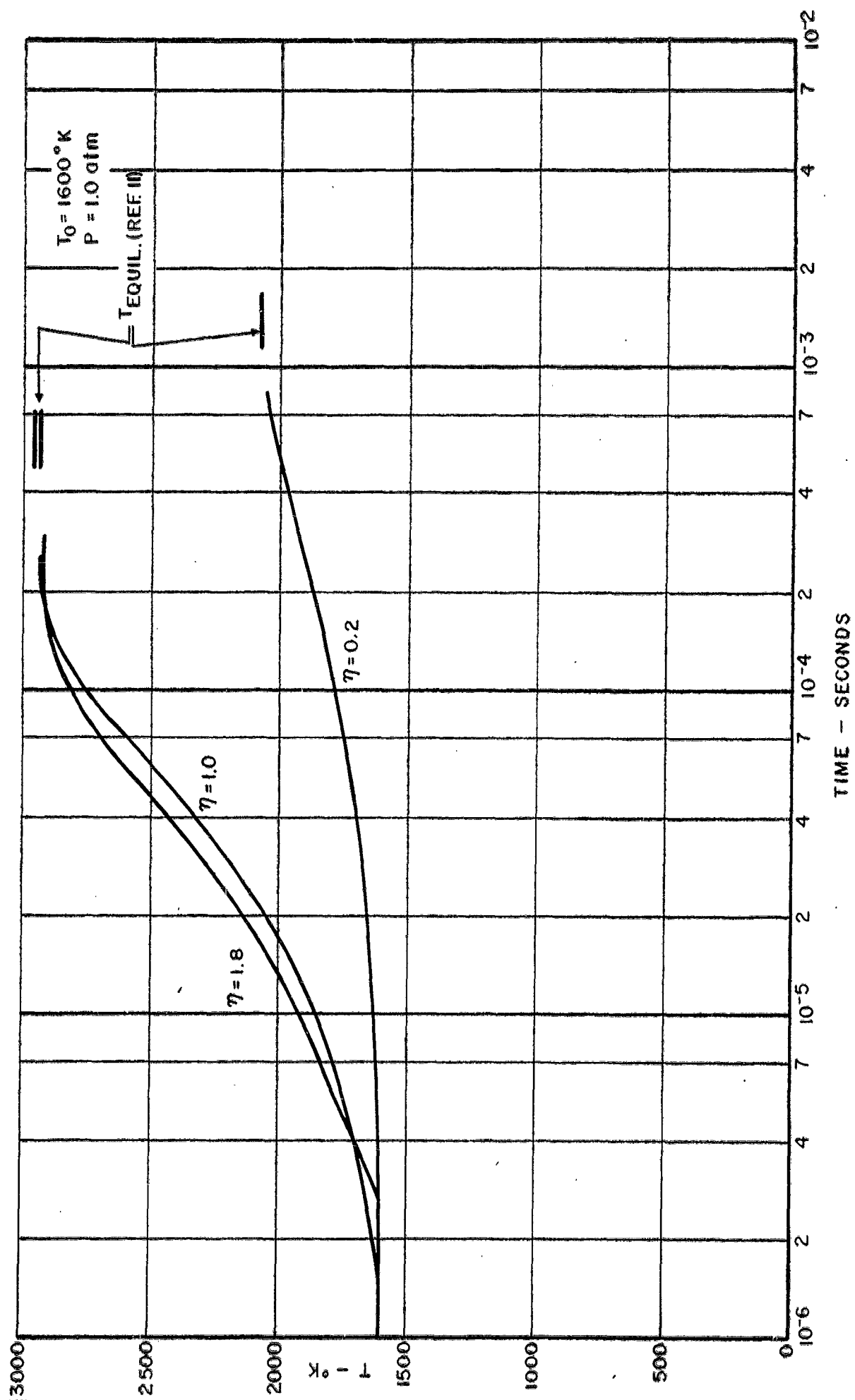


FIG. 1 TEMPERATURE HISTORY  
 c) CASES 5-7



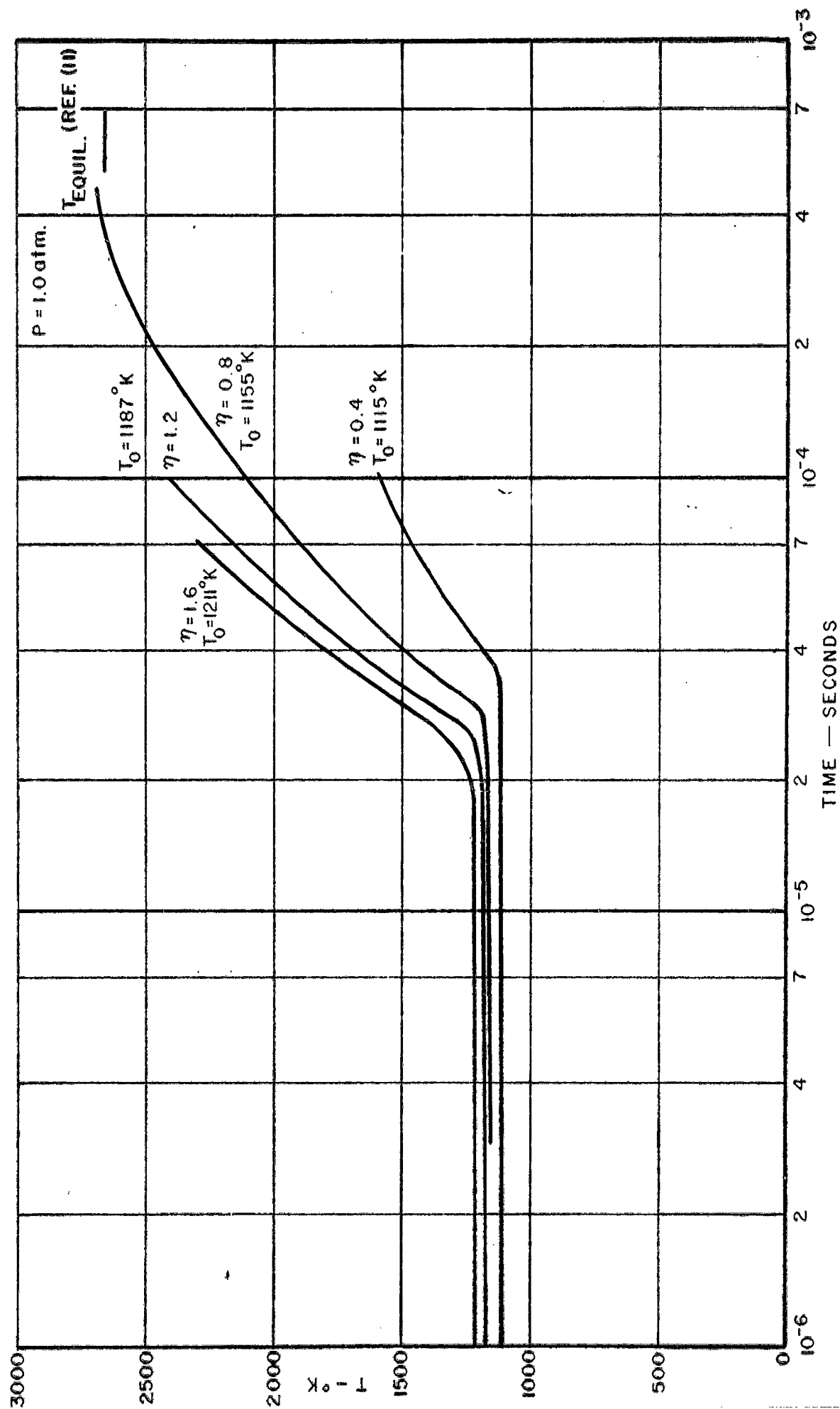


FIG. 1 TEMPERATURE HISTORY

d) CASES 8-II

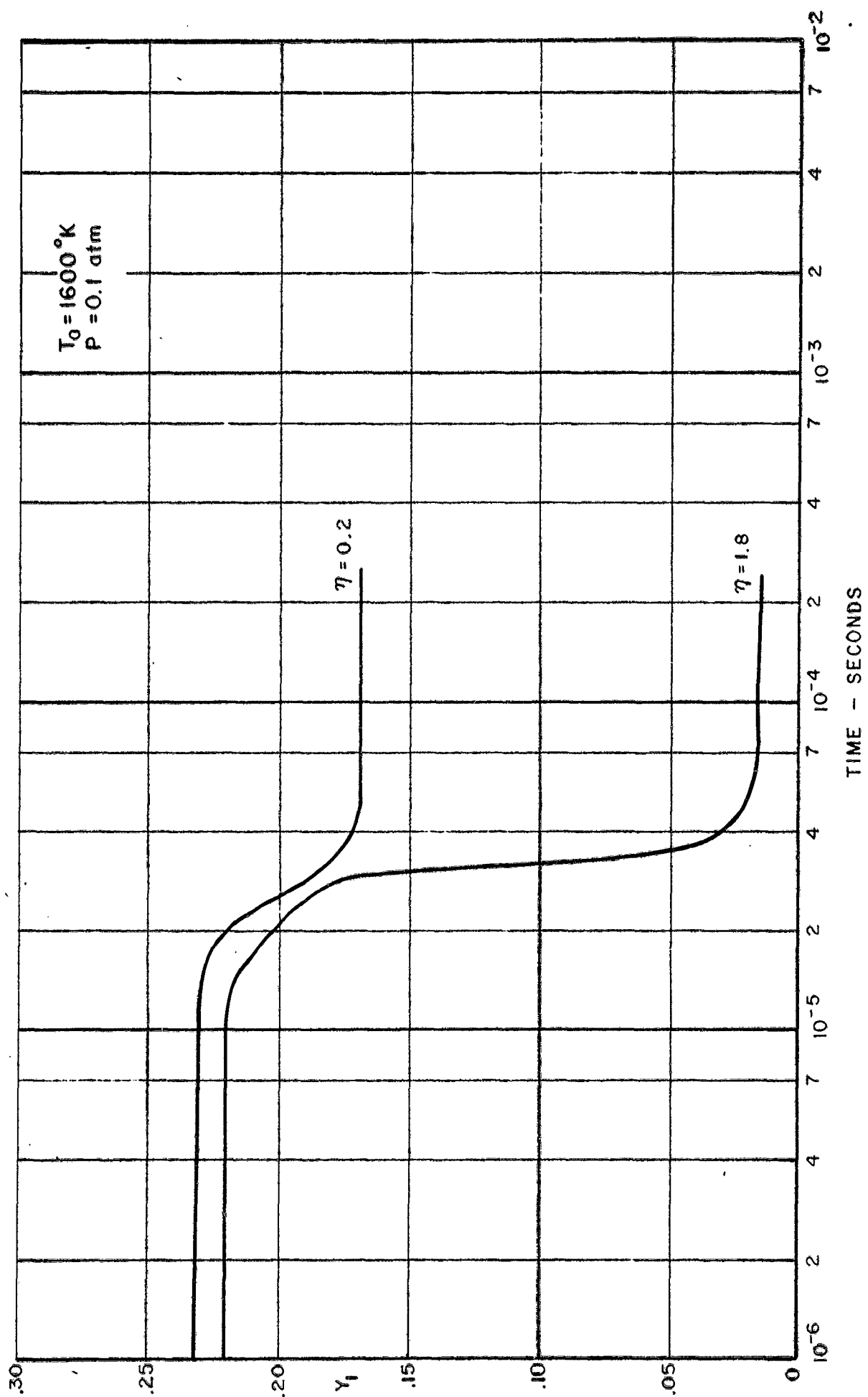


FIG. 2 HISTORY OF THE MASS FRACTION OF MOLECULAR OXYGEN  
 a) CASES 1 AND 2

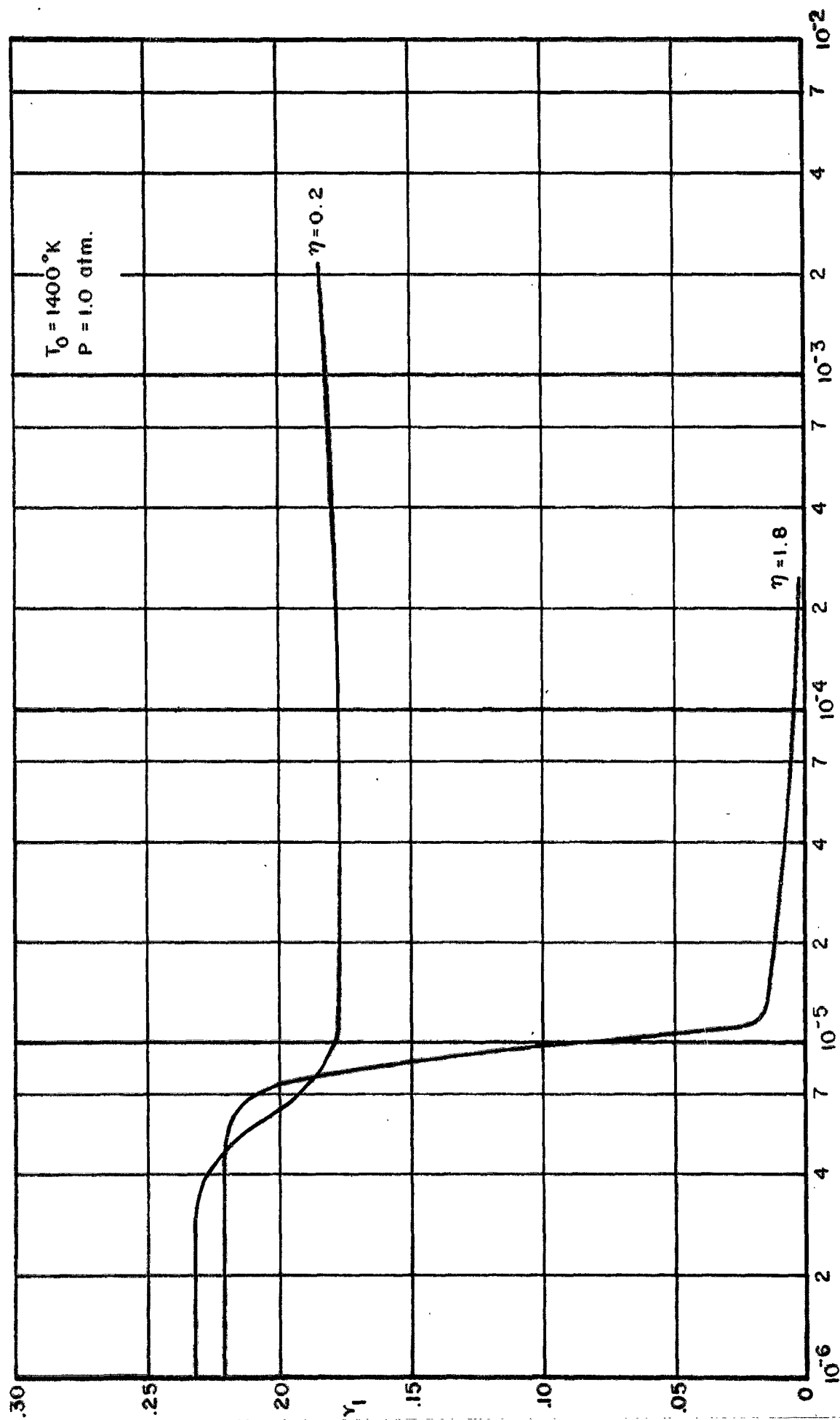


FIG. 2 HISTORY OF THE MASS FRACTION OF MOLECULAR OXYGEN  
b) CASES 3 AND 4

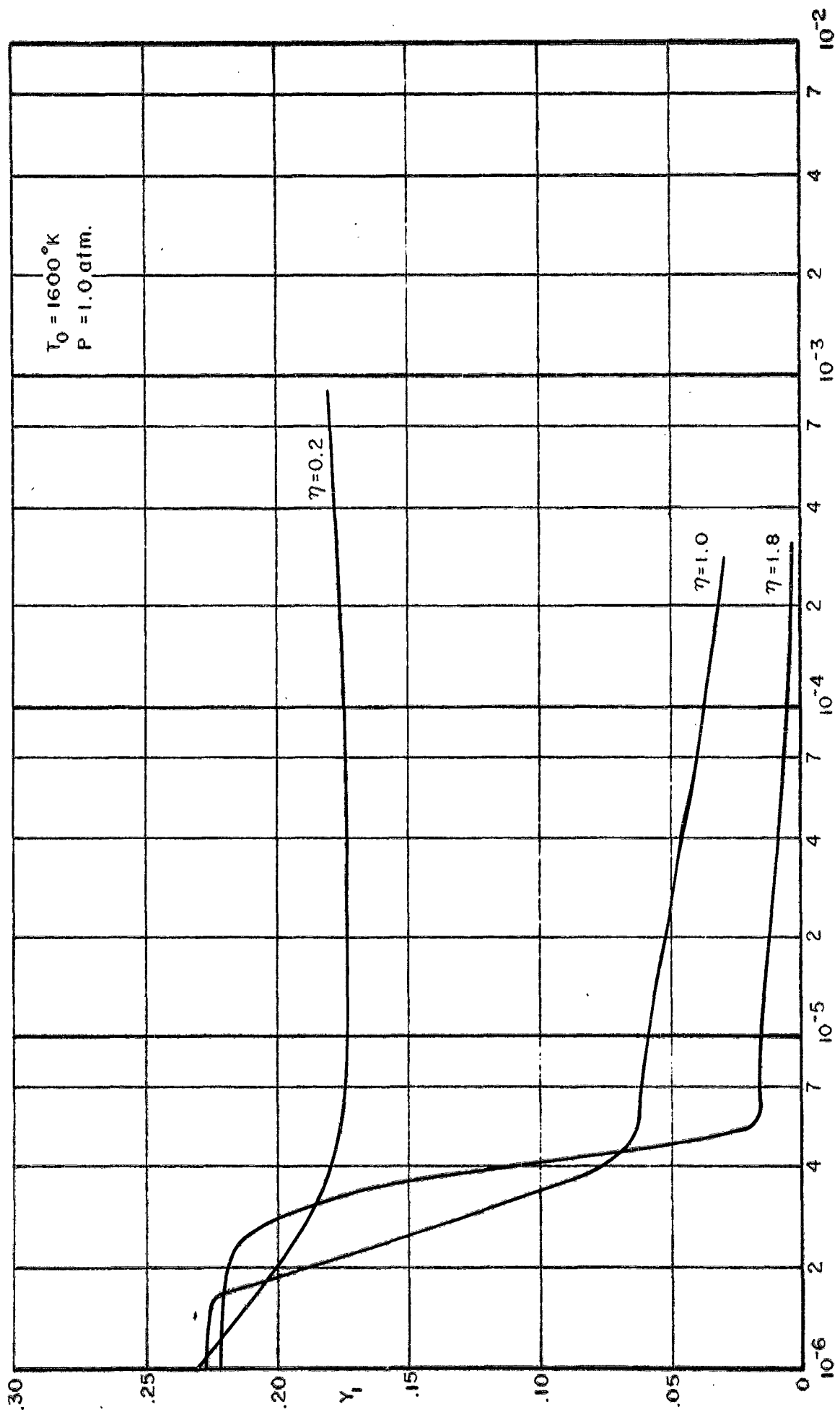
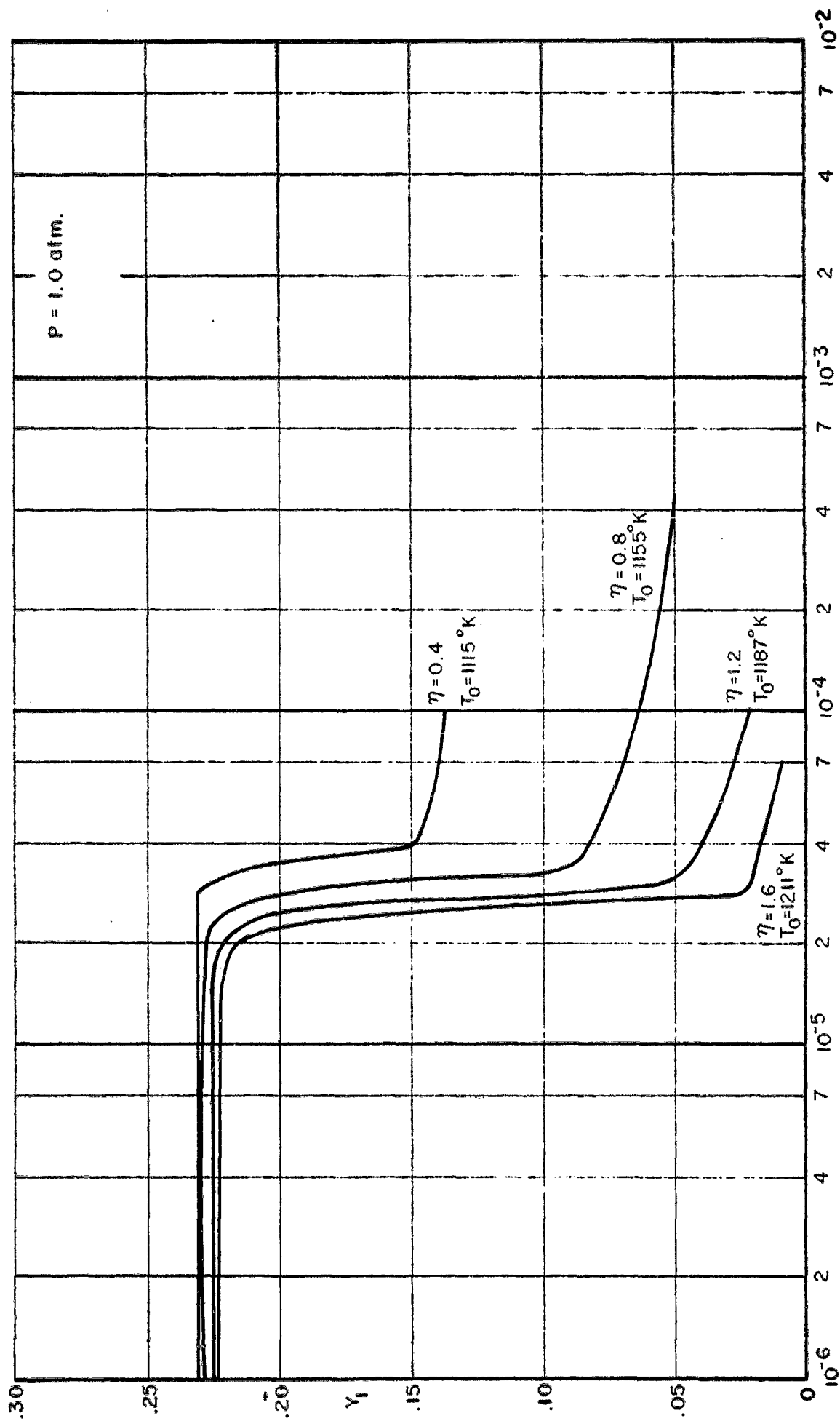


FIG. 2 HISTORY OF THE MASS FRACTION OF MOLECULAR OXYGEN  
c) CASES 5-7



TIME - SECONDS

FIG. 2 HISTORY OF THE MASS FRACTION OF MOLECULAR OXYGEN

d) CASES 8 - 11

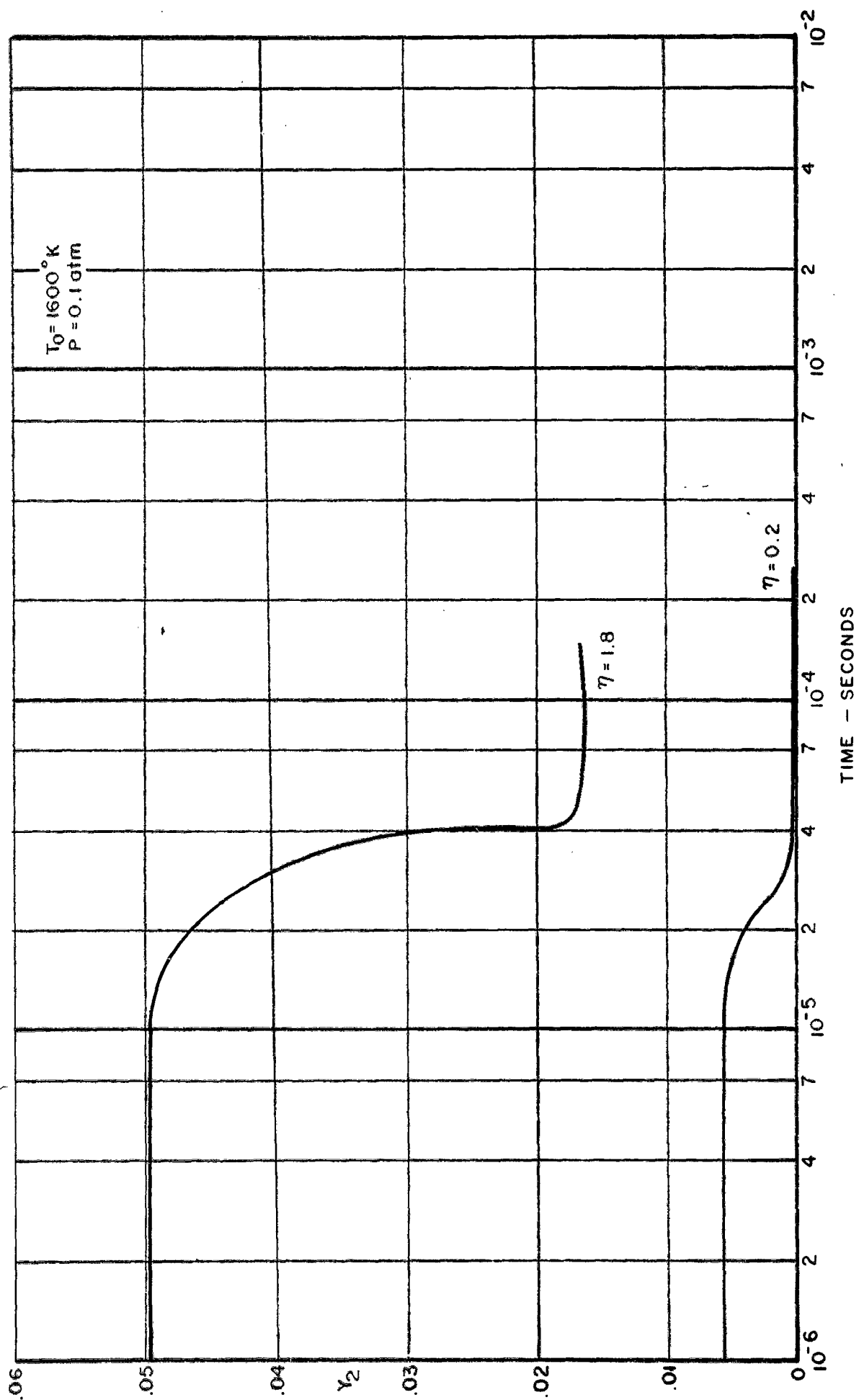


FIG. 3 HISTORY OF THE MASS FRACTION OF MOLECULAR HYDROGEN

a) CASES 1 AND 2

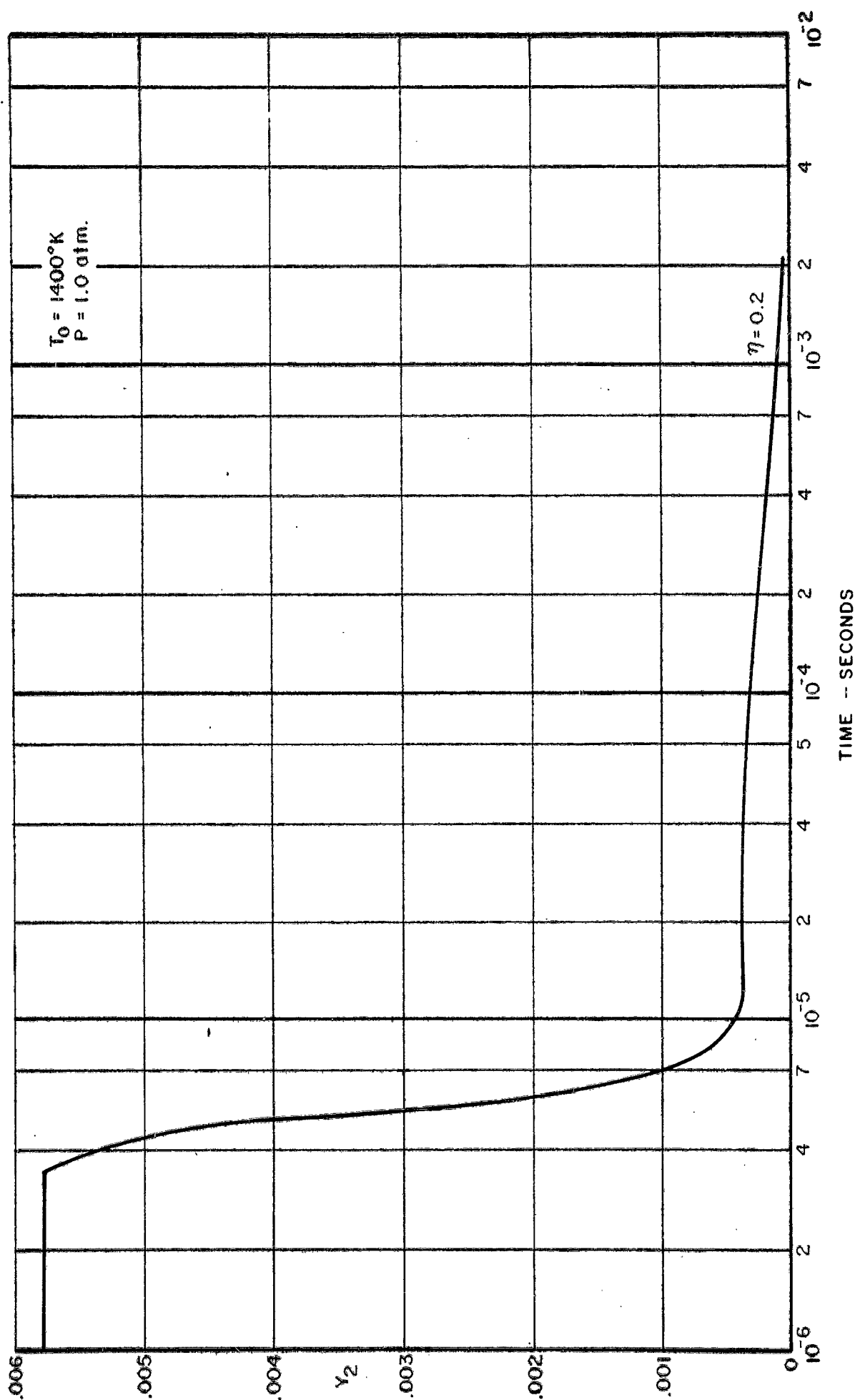


FIG. 3 HISTORY OF THE MASS FRACTION OF MOLECULAR HYDROGEN  
b) CASE 3

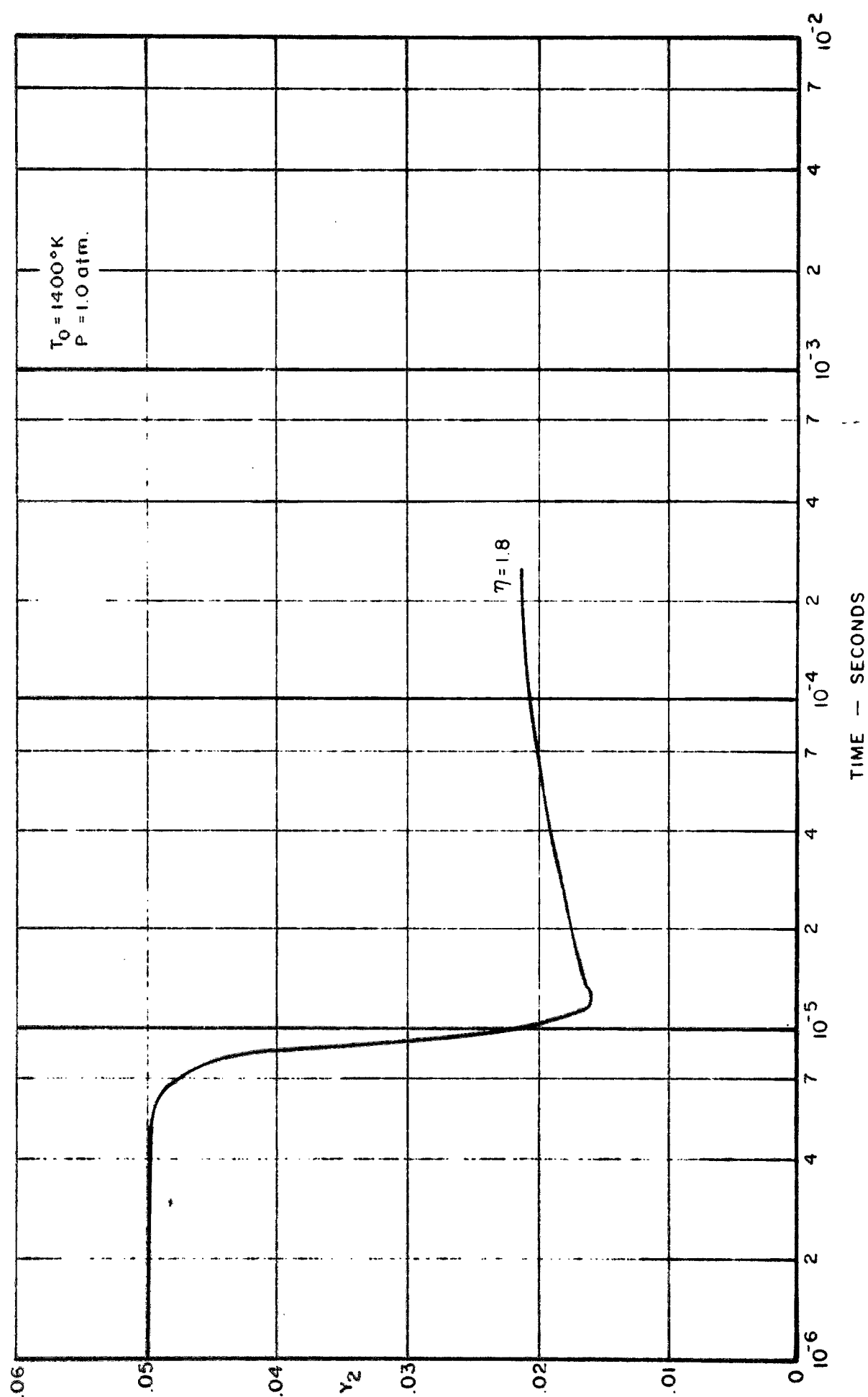


FIG. 3 HISTORY OF THE MASS FRACTION OF MOLECULAR HYDROGEN  
 b) CASE 4



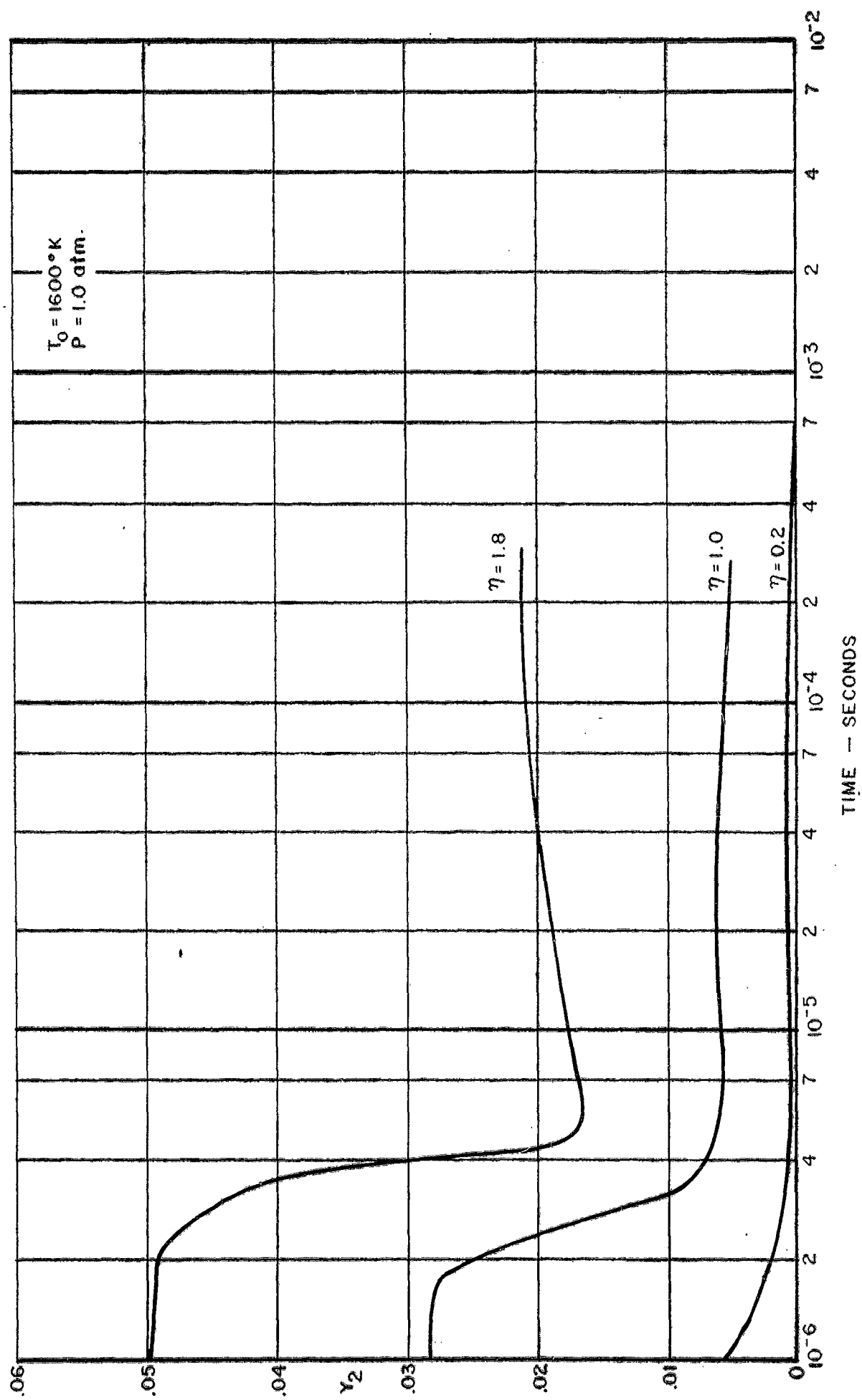


FIG. 3 HISTORY OF THE MASS FRACTION OF MOLECULAR HYDROGEN  
c) CASES 5 - 7

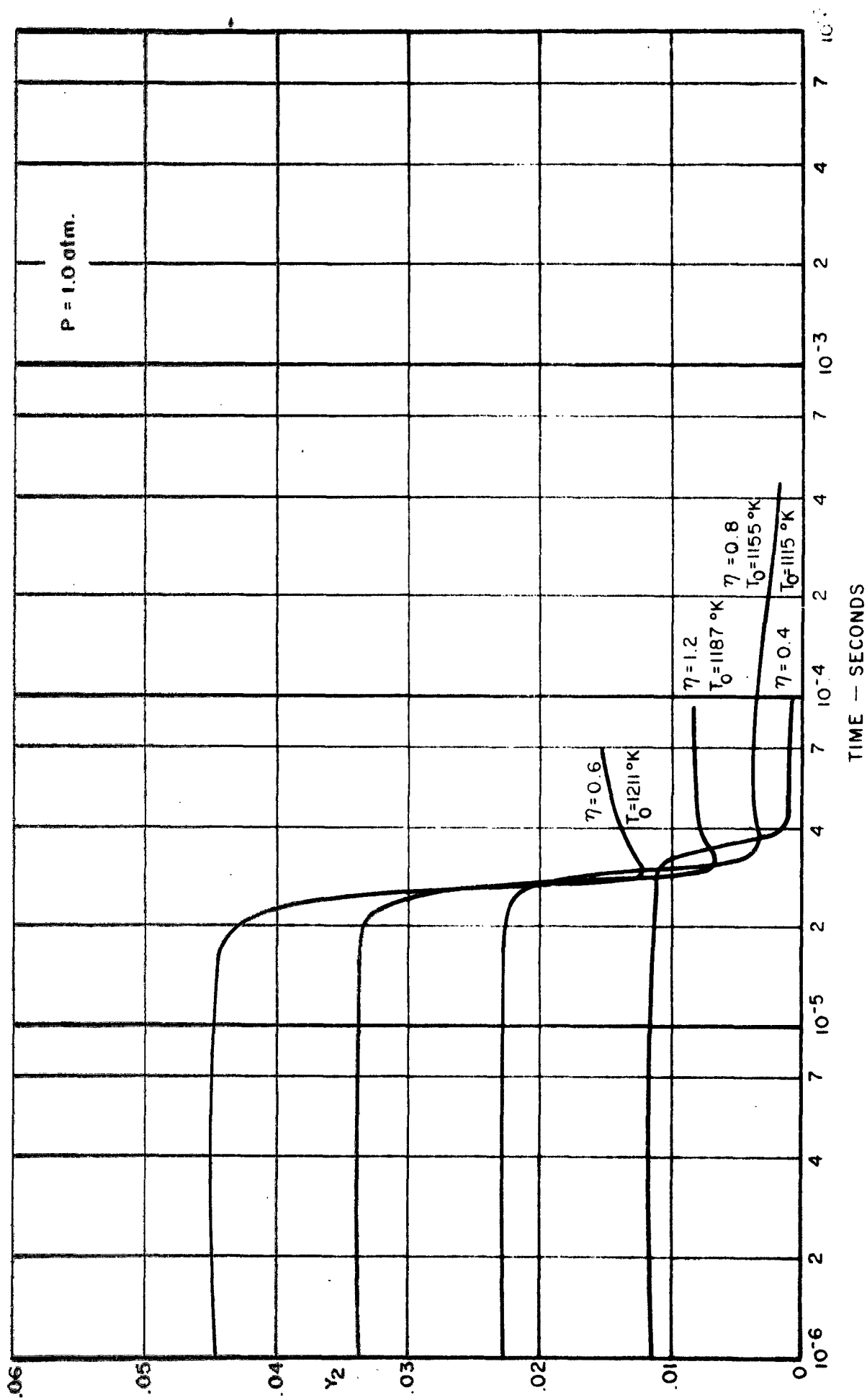


FIG. 3 HISTORY OF THE MASS FRACTION OF MOLECULAR HYDROGEN

d) CASES 8-II

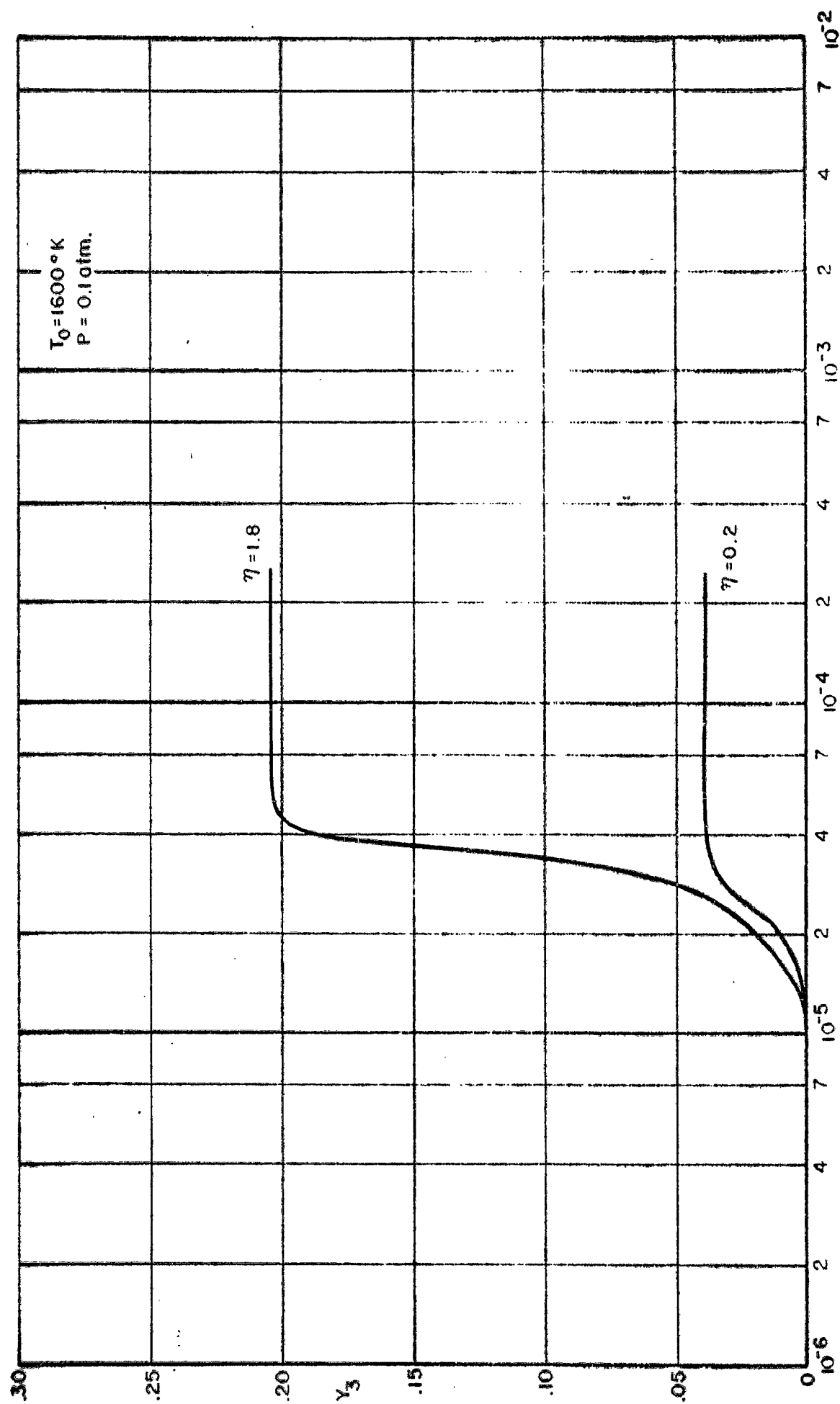


FIG. 4 HISTORY OF THE MASS FRACTION OF WATER  
 a) CASES 1 AND 2

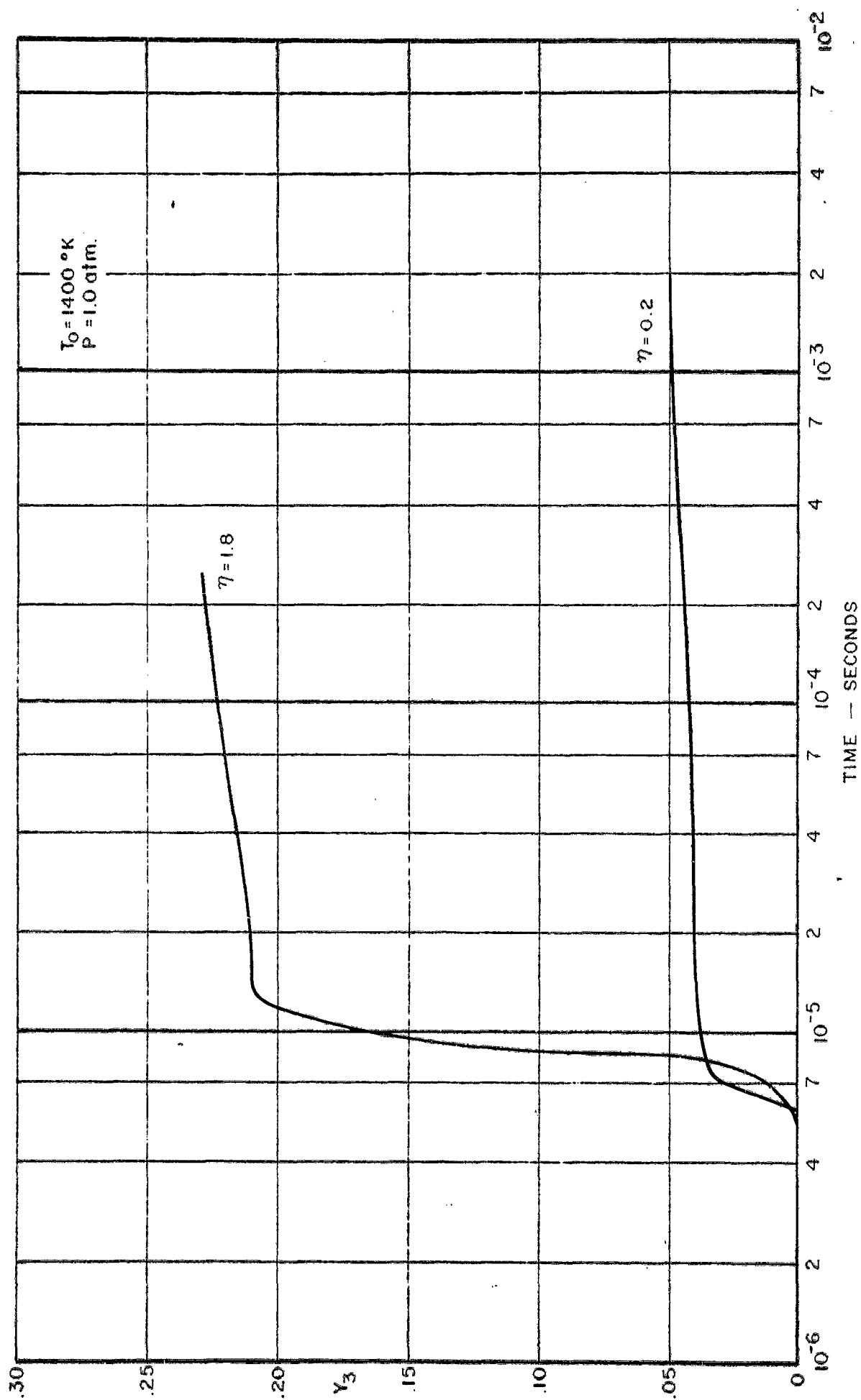


FIG. 4 HISTORY OF THE MASS FRACTION OF WATER

b) CASES 3 AND 4

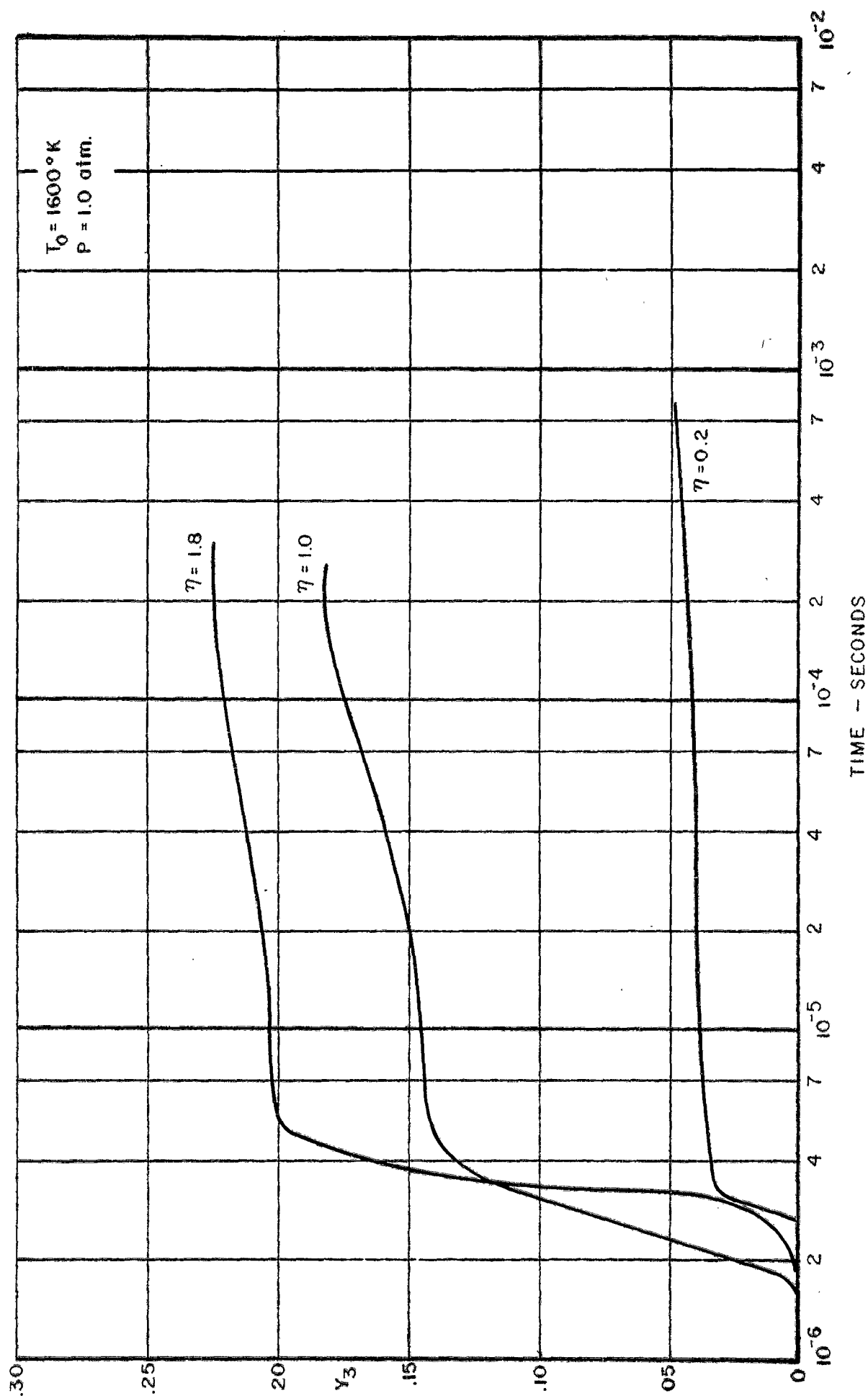


FIG 4 HISTORY OF THE MASS FRACTION OF WATER  
c) CASES 5-7

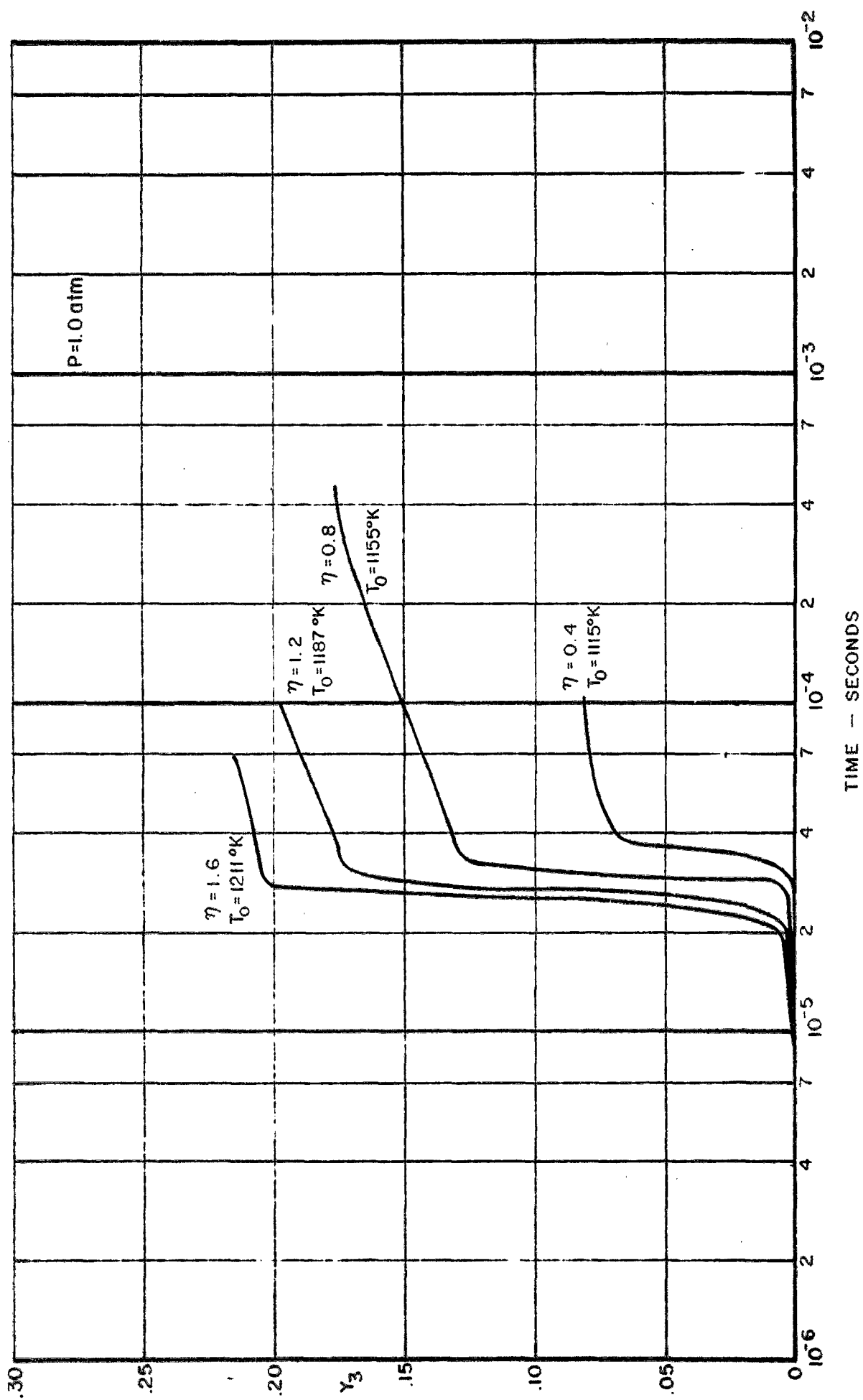


FIG. 4 HISTORY OF THE MASS FRACTION OF WATER  
d) CASES 8-II

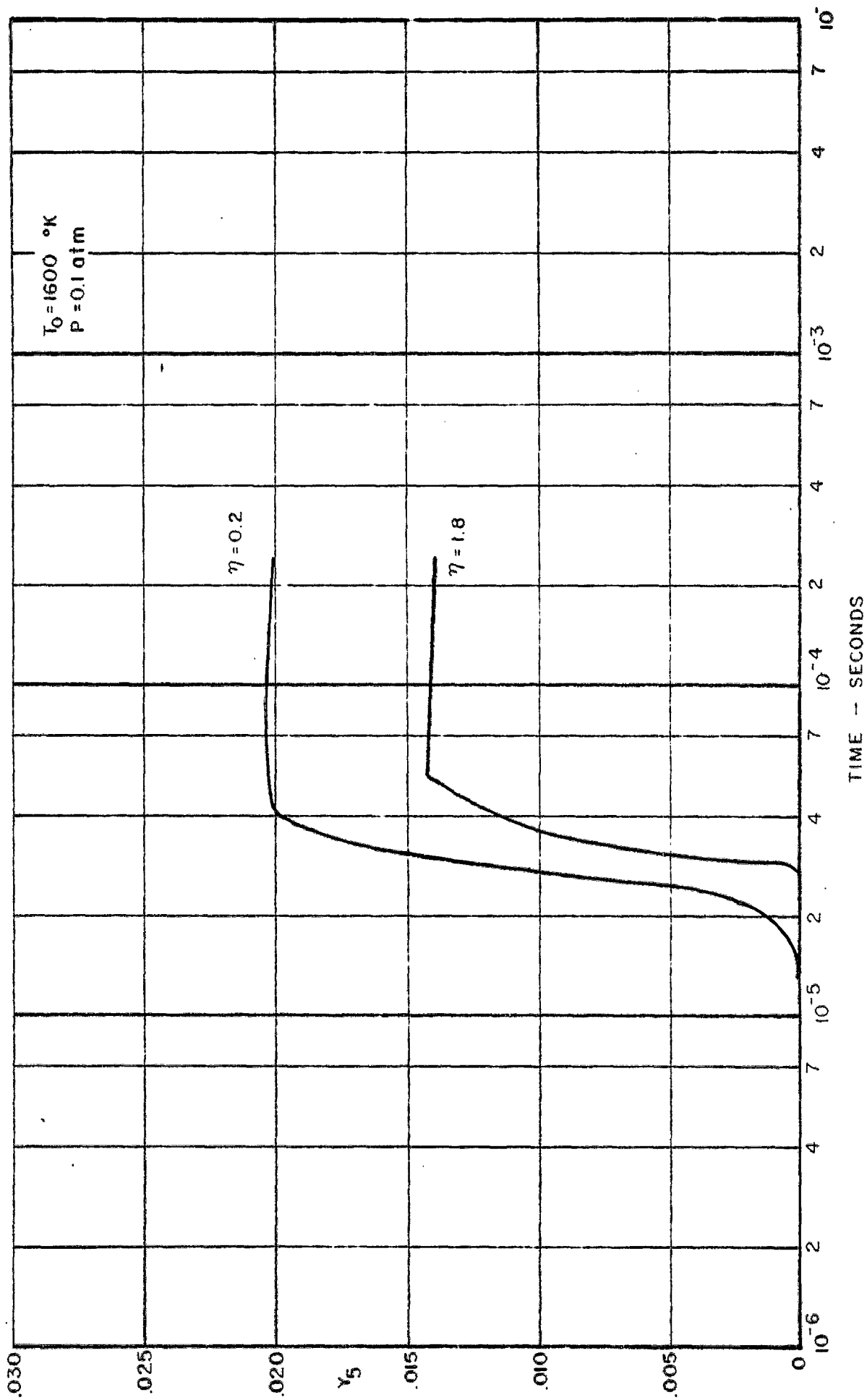


FIG. 1.5 HISTORY OF THE MASS FRACTION OF ATOMIC OXYGEN

a) CASES 1 AND 2

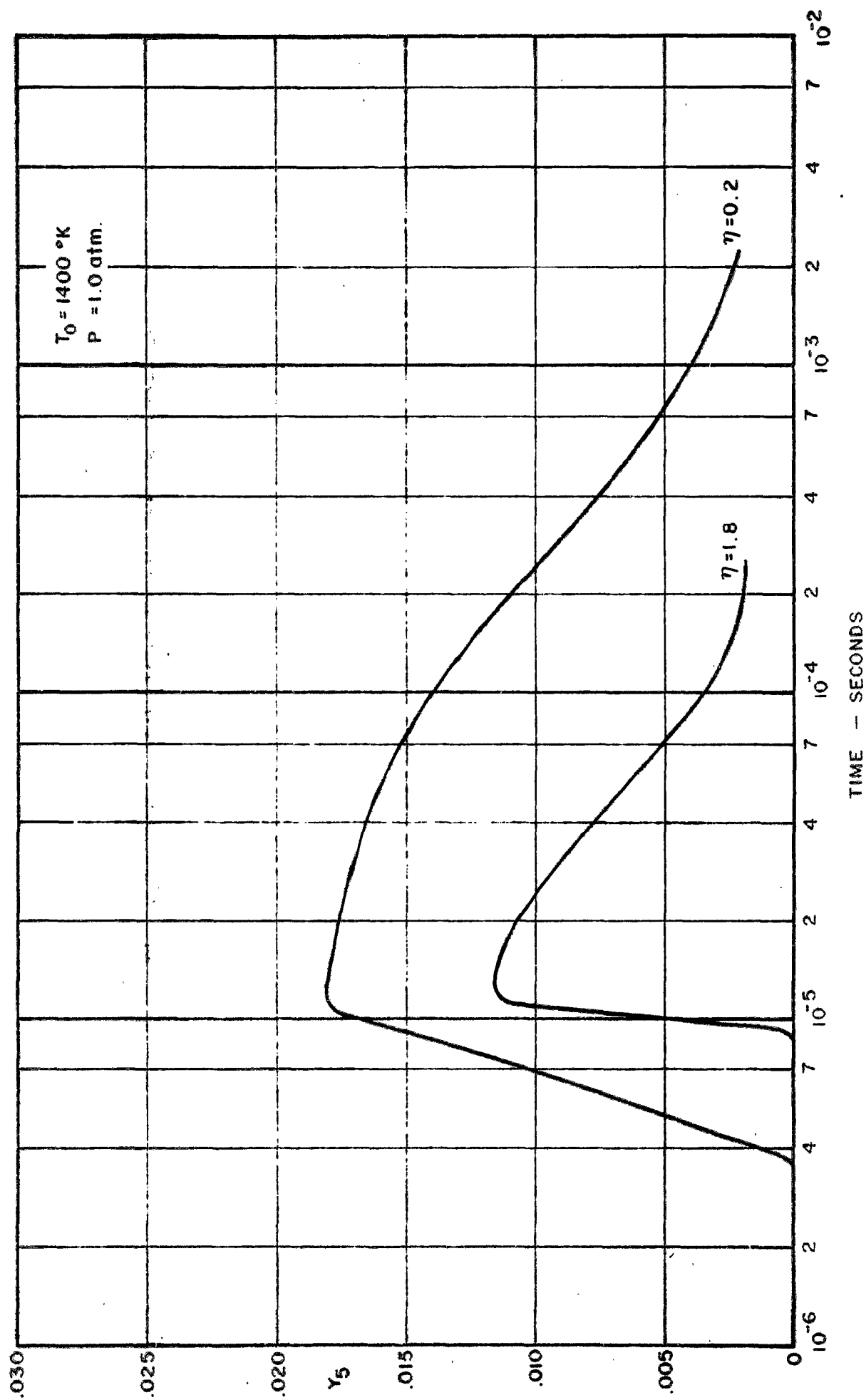


FIG. 5 HISTORY OF THE MASS FRACTION OF ATOMIC OXYGEN  
 b) CASES 3 AND 4



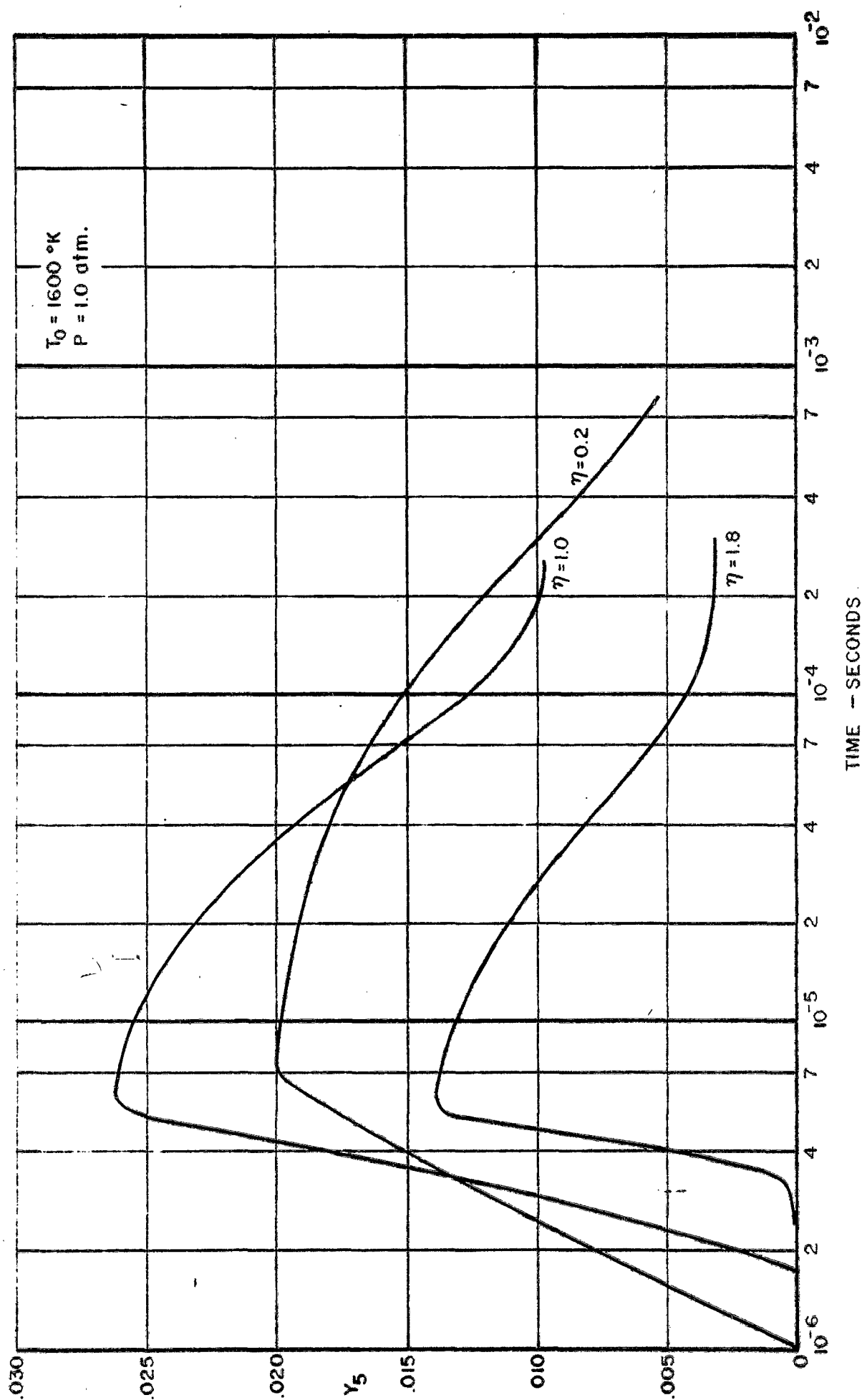


FIG. 5 HISTORY OF THE MASS FRACTION OF ATOMIC OXYGEN

c) CASES 5-7

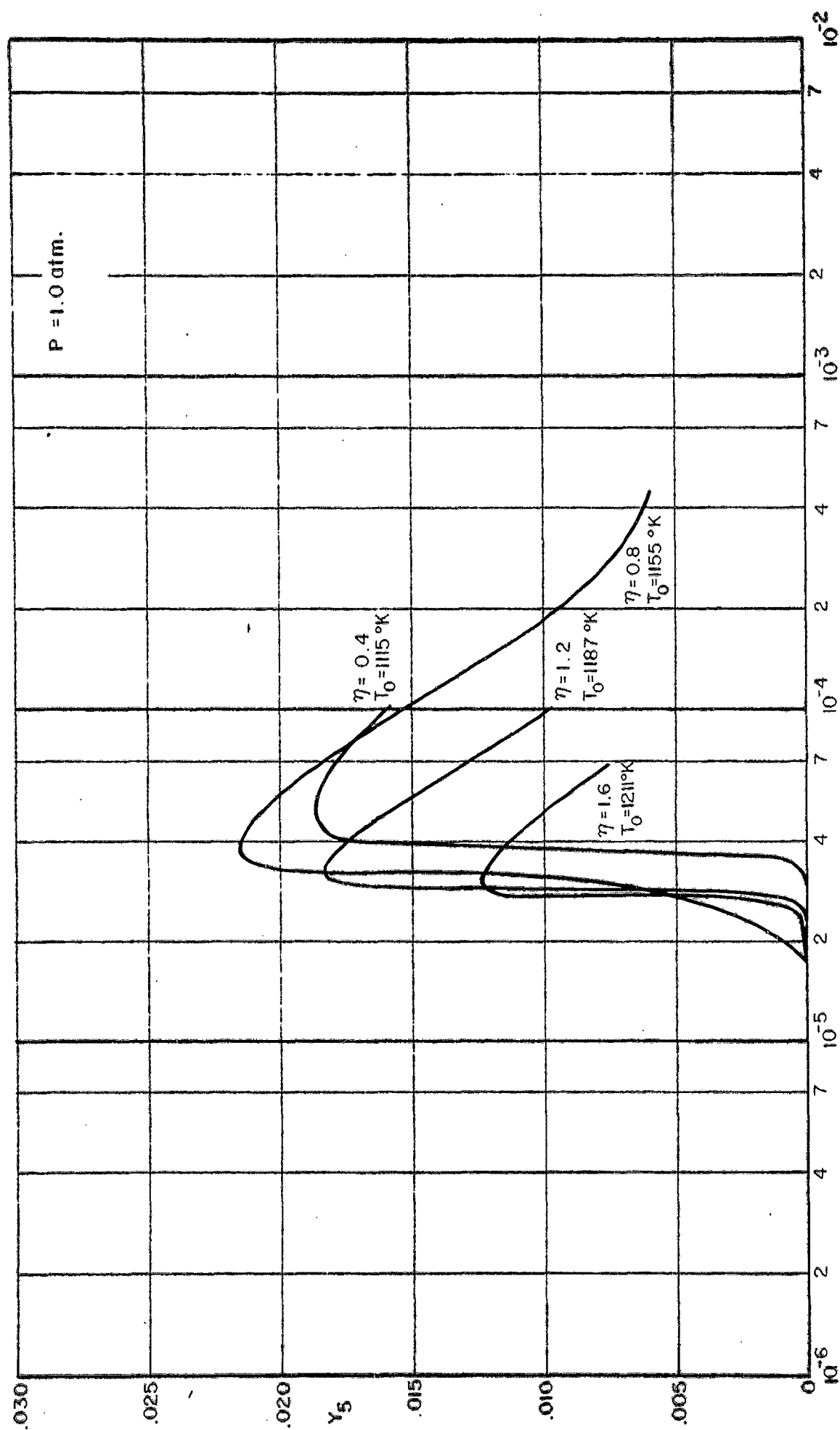


FIG. 5 HISTORY OF THE MASS FRACTION OF ATOMIC OXYGEN

d) CASES 8 - 11

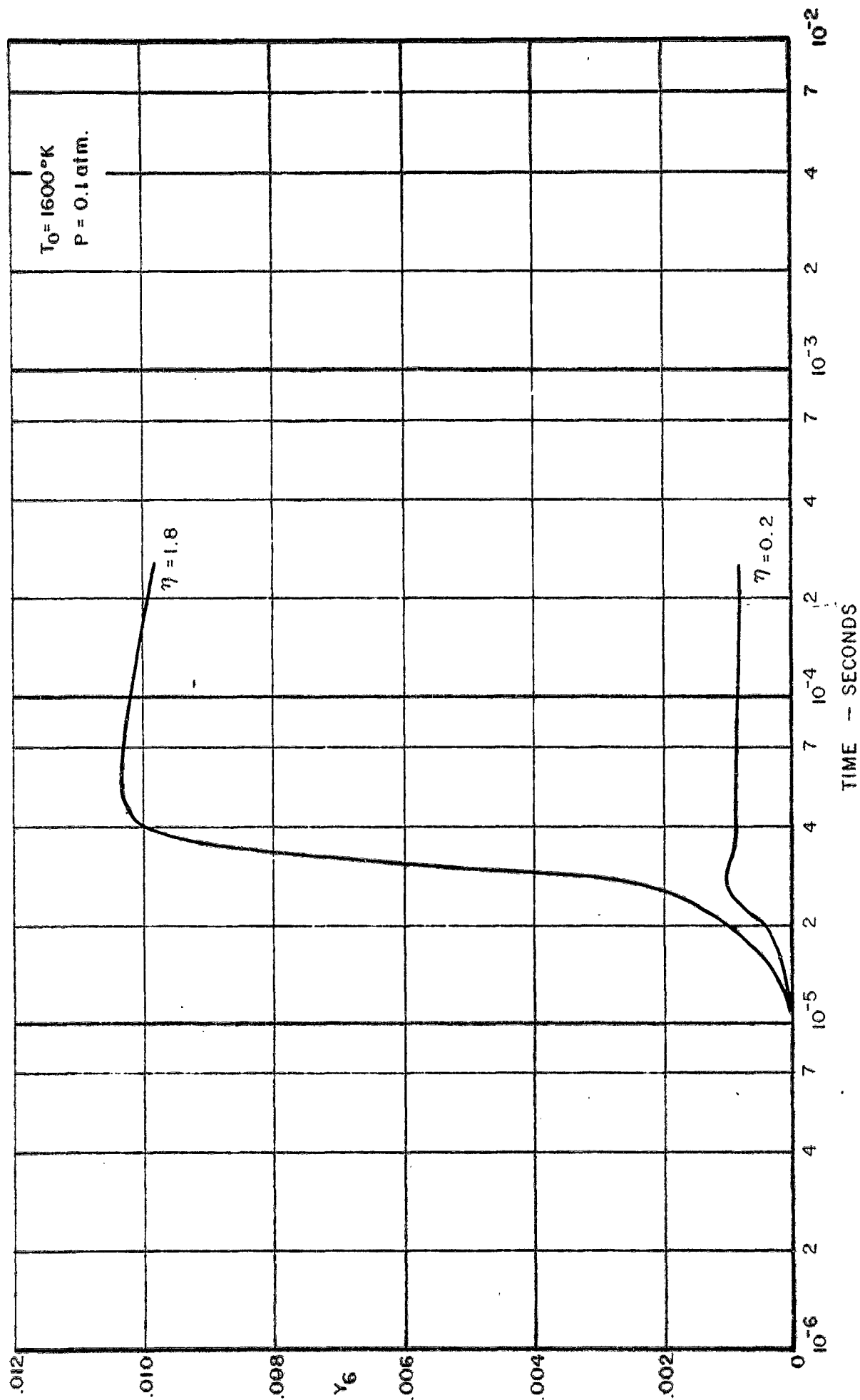


FIG. 6 HISTORY OF THE MASS FRACTION OF ATOMIC HYDROGEN  
a) CASES 1 AND 2

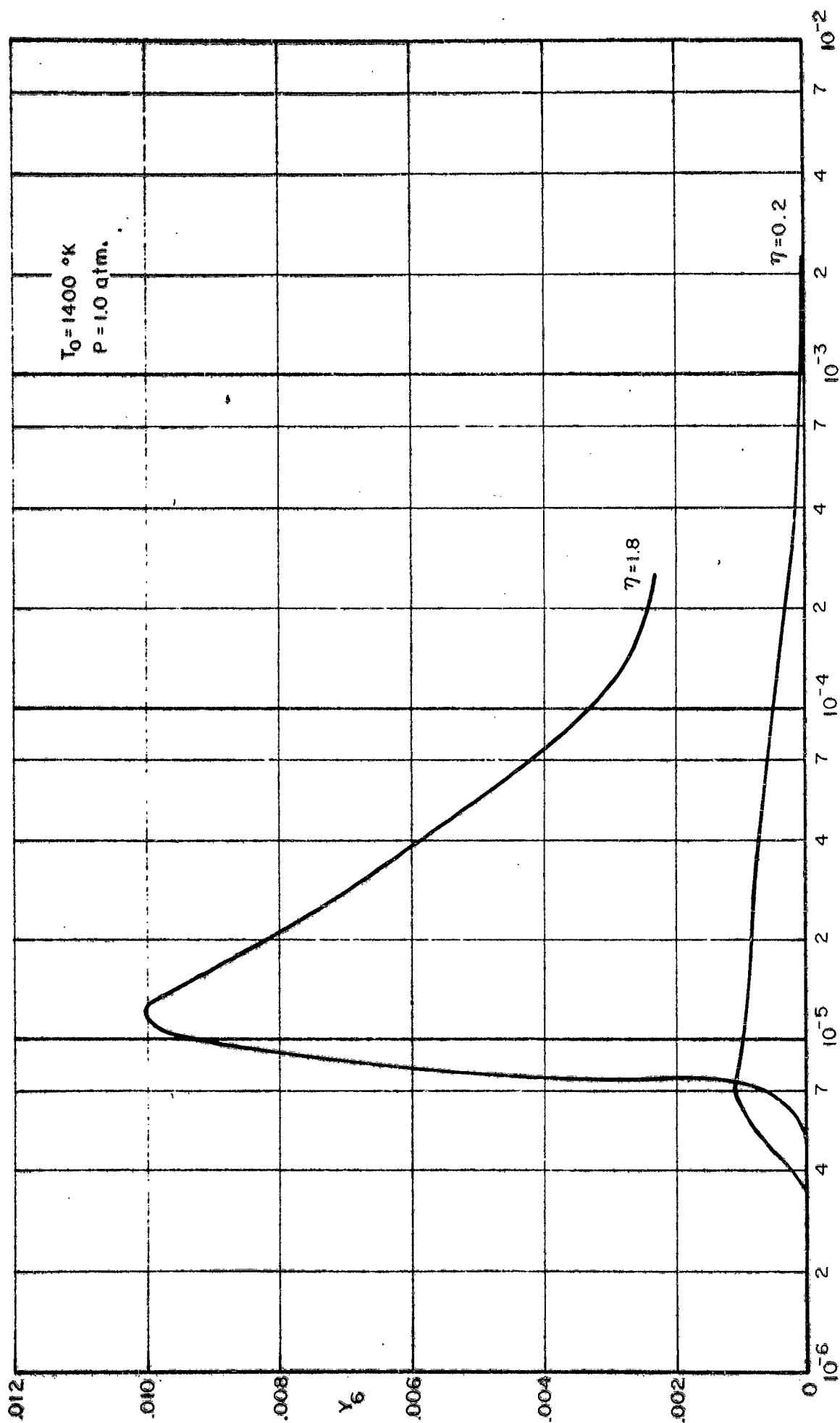


FIG. 6 HISTORY OF THE MASS FRACTION OF ATOMIC HYDROGEN  
b) CASES 3 AND 4

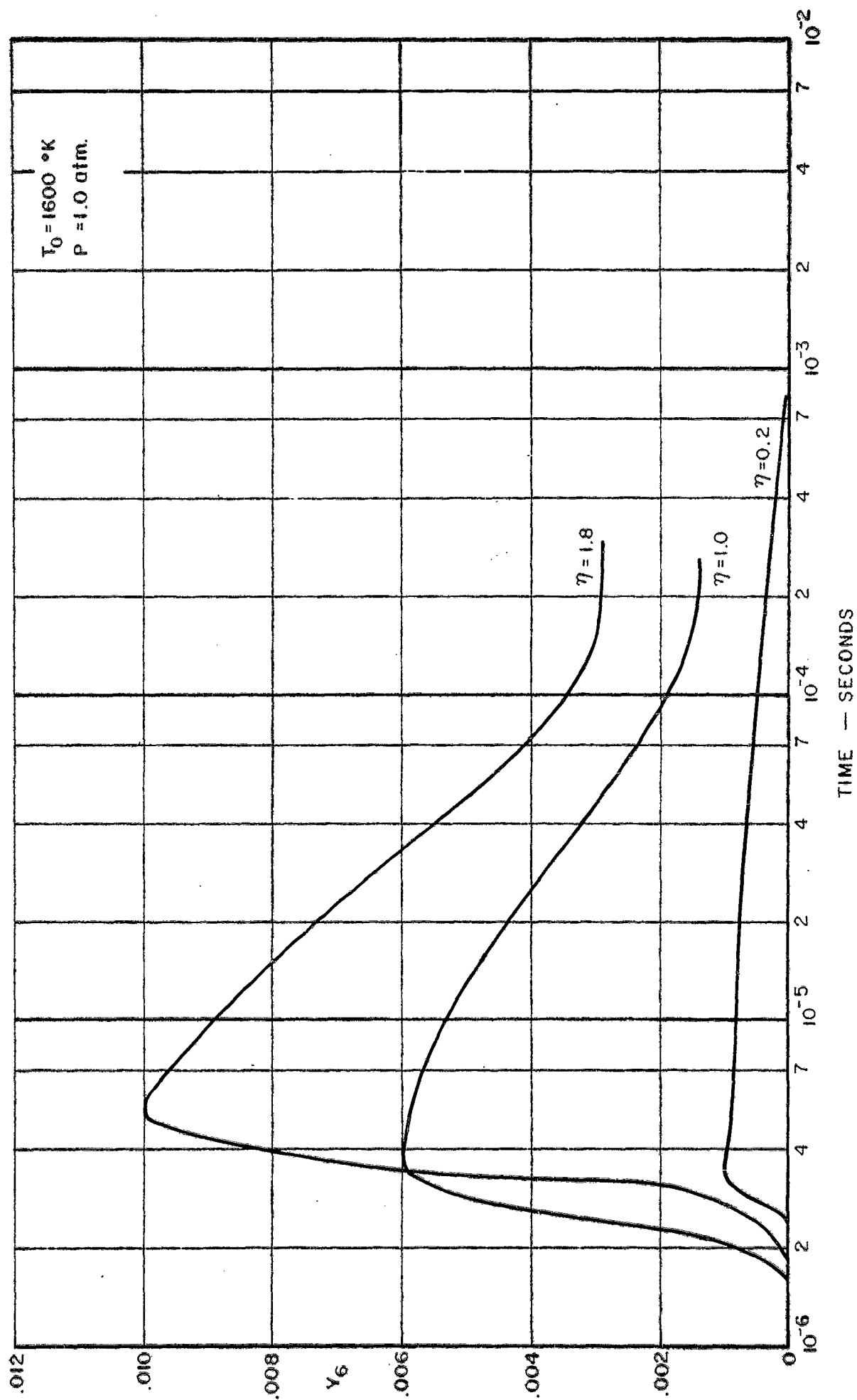


FIG. 6. HISTORY OF THE MASS FRACTION OF ATOMIC HYDROGEN

c) CASES 5 - 7

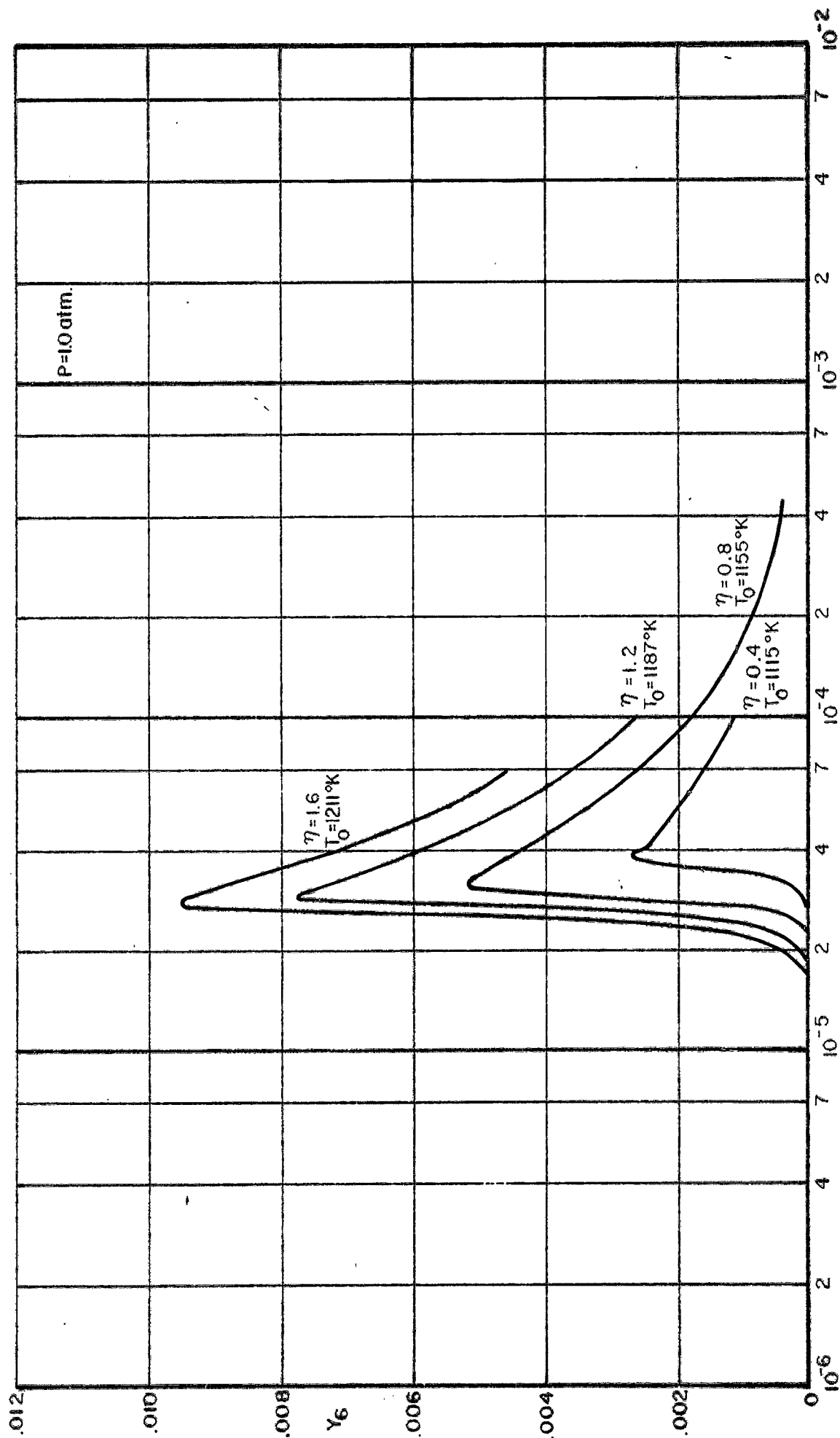


FIG. 6 HISTORY OF THE MASS FRACTION OF ATOMIC HYDROGEN  
d) CASES 8-II

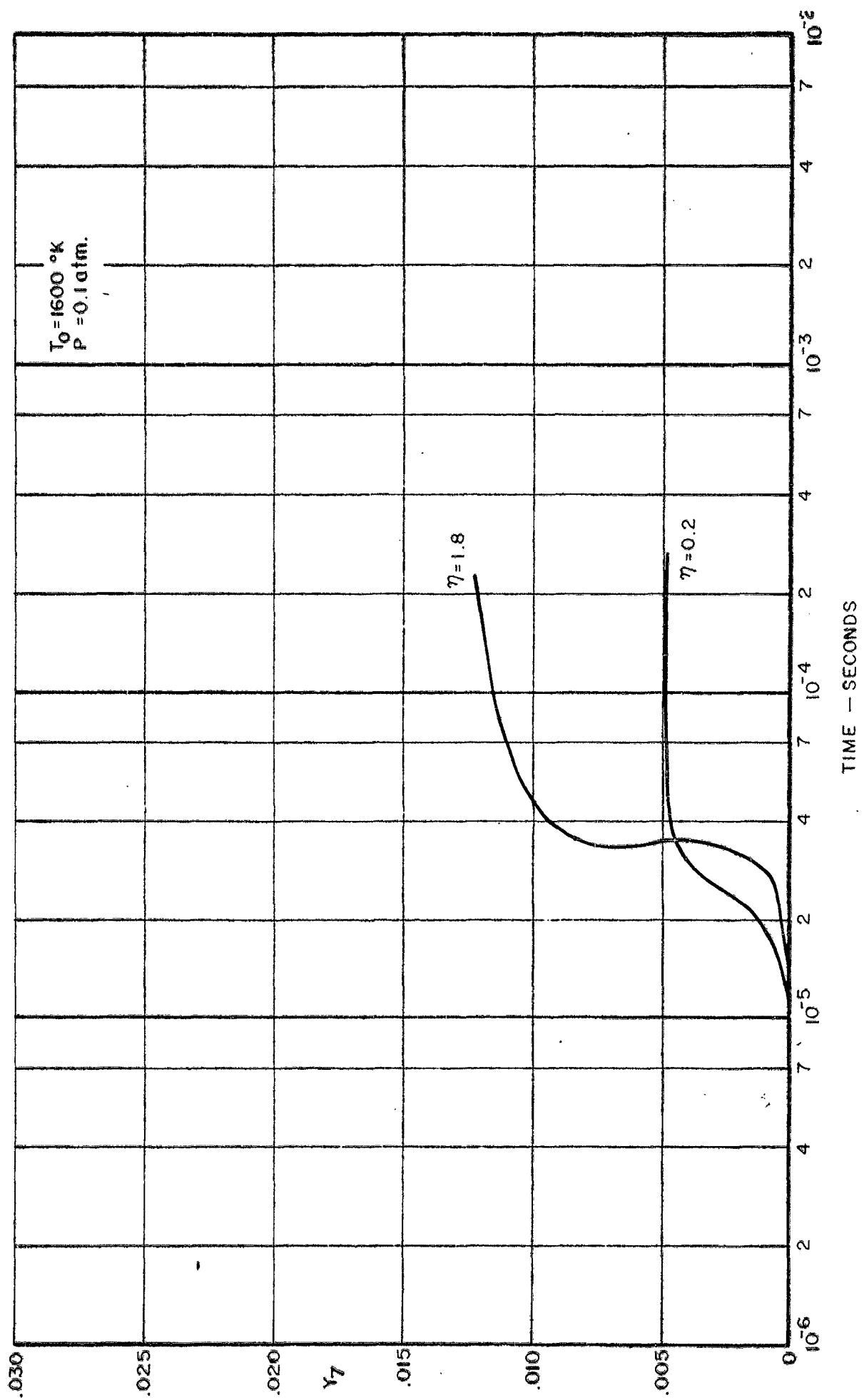


FIG. 7 HISTORY OF THE MASS FRACTION OF THE HYDROXYL RADICAL  
a) CASES 1 AND 2

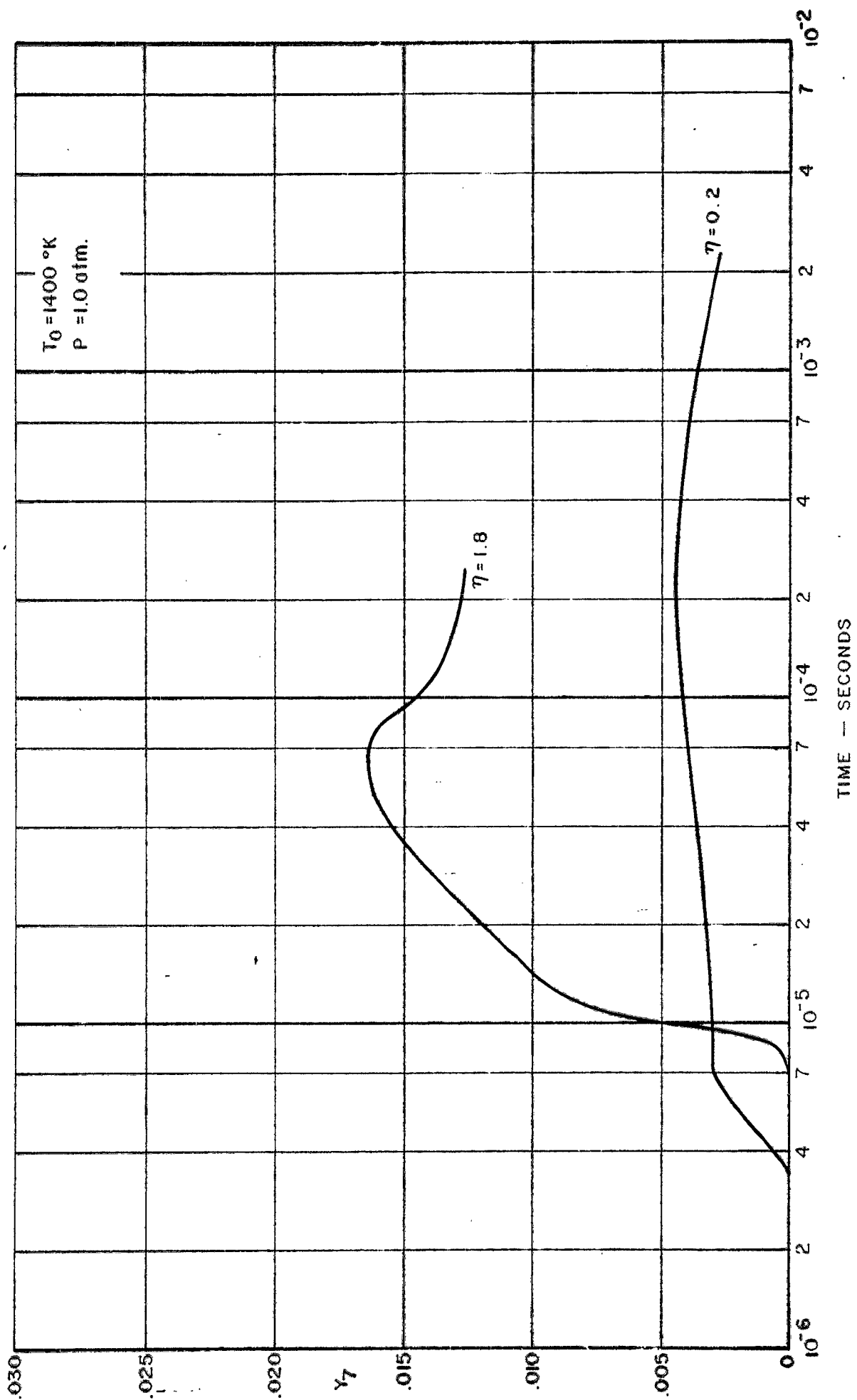


FIG. 7 HISTORY OF THE MASS FRACTION OF THE HYDROXYL RADICAL

b) CASES 3 AND 4



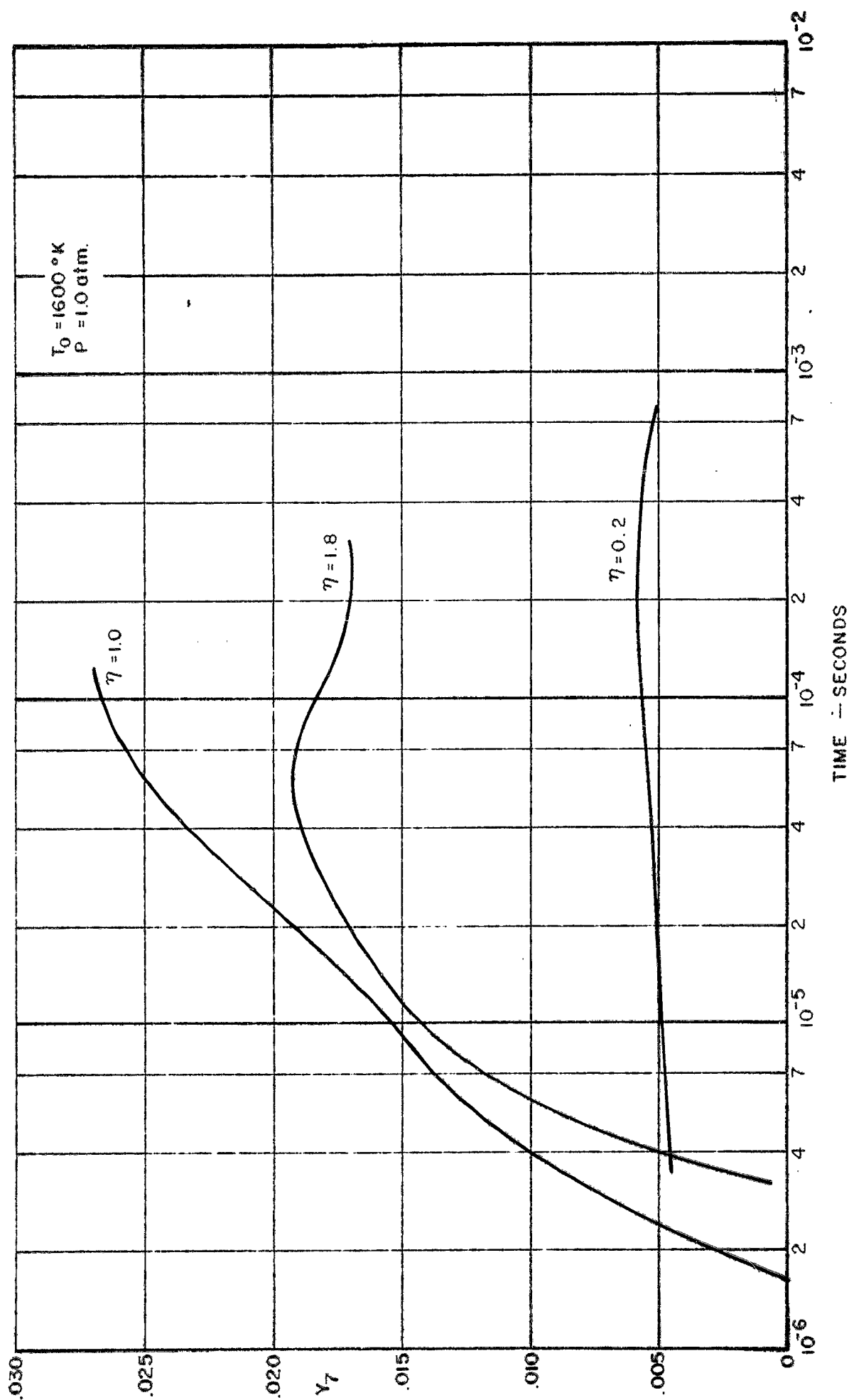


FIG. 7 HISTORY OF THE MASS FRACTION OF THE HYDROXYL RADICAL

c) CASES 5-7

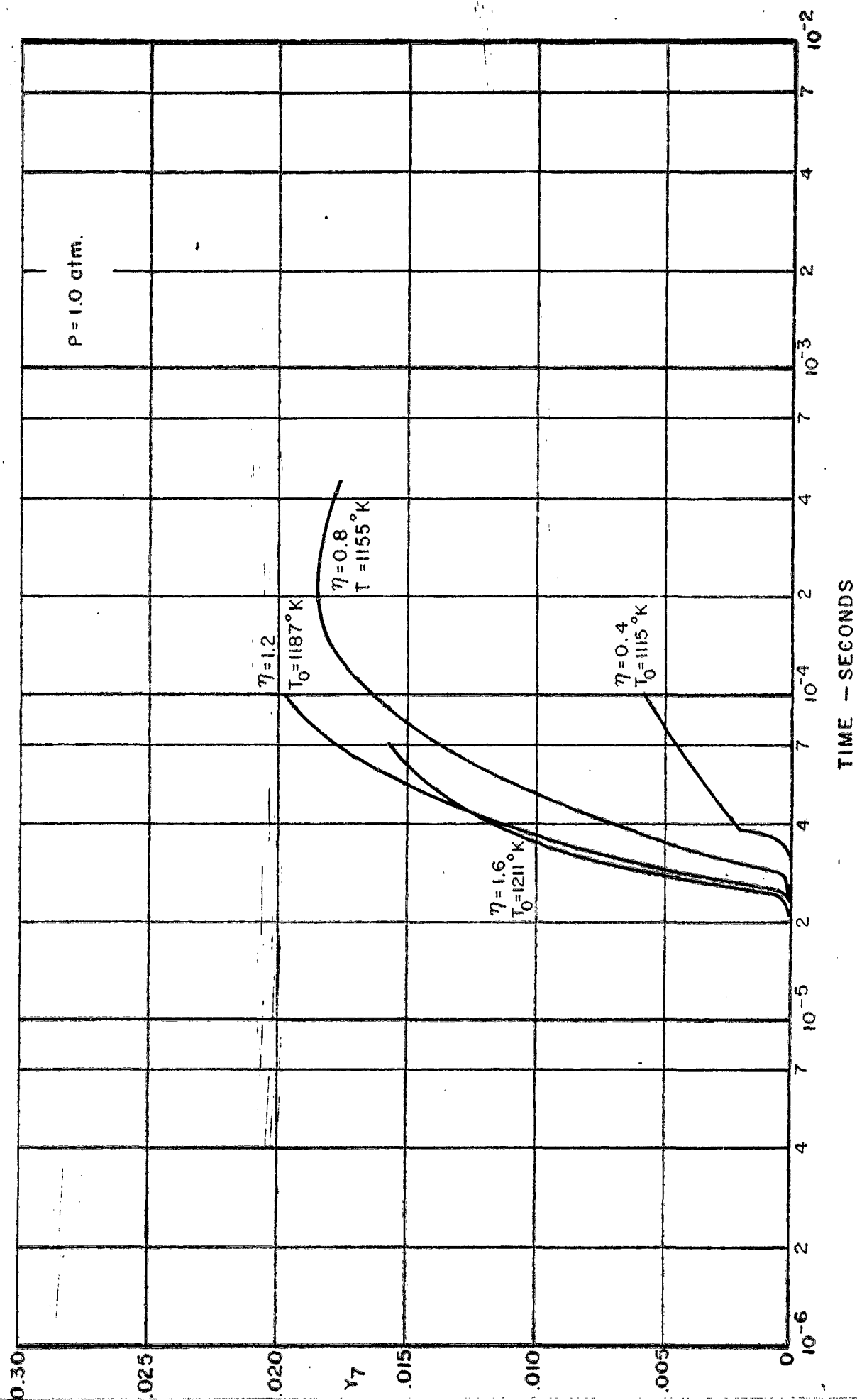


FIG. 7 HISTORY OF THE MASS FRACTION OF THE HYDROXYL RADICAL  
d) CASES 8 - 11

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